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# On the Longitude Effect of Cosmic Radiation

M. S. VALLARTA, *Massachusetts Institute of Technology*
(Received February 26, 1935)

It is shown that if the equivalent magnetic dipole describing the earth's magnetic field at large distances is placed at the magnetic center of the earth as calculated by Schmidt, the theory of the latitude and azimuthal effects developed by Lemaitre and Vallarta also accounts for the longitude effect found by Clay, van Alphen and Hooft and, independently, by Millikan and Neher. Further it is shown that if the distribution function of magnetically deflectable particles capable of reaching the earth's tropical belt is substantially an exponentially decreasing function of their energy, the theory quantitatively agrees with experiment.

CLAY, van Alphen and Hooft[1] and, independently, Millikan and Neher[2] have found experimentally that the total intensity of cosmic radiation measured by an ionization chamber at sea level is different for the same geomagnetic latitude and different longitudes. They have suggested that this longitude effect is to be interpreted as due to an asymmetry of the earth's magnetic field about the earth's center. The purpose of this note is to examine this point of view in the light of the theory of the latitude and azimuthal effects developed by Lemaitre and Vallarta,[3] and to find out what conclusions can be drawn from the experimental data concerning the energy distribution function of magnetically deflectable particles capable of reaching the tropical belt.

The magnetic field at the surface of the earth (and elsewhere) can be represented by an expansion of Legendre polynomials about any arbitrary point chosen as origin, in particular about the center of the geoid, but as Schmidt[4] has pointed out the expansion takes a particularly simple form, only one term of the first order and one of the second remaining if the origin is chosen at the magnetic center of the earth, a point about 300 km from the center of the geoid at geographic coordinates lat. 10 N, long. 168 E. If the equivalent magnetic dipole is placed not at the center of the geoid, but at the magnetic center of the earth with its axis pointing towards the geomagnetic poles, the immediate consequence is that the distance from the geomagnetic equator, or from any geomagnetic parallel, to the dipole is a periodic function of longitude. Since changing the distance to the dipole also changes the opening of the allowed cone[5] for any given energy, one must

[1] J. Clay, P. M. van Alphen and C. G.'t Hooft, Physica **1**, 829 (1934).
[2] R. A. Millikan and H. V. Neher, Phys. Rev. **47**, 205 (1935).
[3] A discussion of the present status of the theory is given in a paper by Lemaitre, Vallarta and Bouckaert, Phys. Rev. **47**, 434 (1935), where full references to previous literature are given.
[4] A. Schmidt, Zeits. f. Geophys. **2**, 38 (1926). The introduction of the actual magnetic field of the earth, using Schmidt's results, as done in the present paper, was already suggested by Lemaitre and Vallarta, reference 6, p. 88, footnote (7).
[5] The theory of the determination of the cone is outlined in reference 3 and more fully discussed in Lemaitre's and in Bouckaert's papers there quoted.

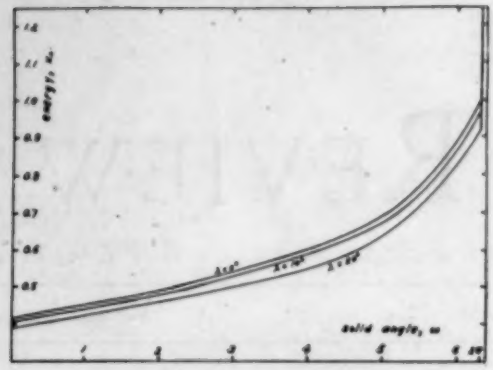

FIG. 1. The solid angle of opening of the cone at three geomagnetic latitudes.

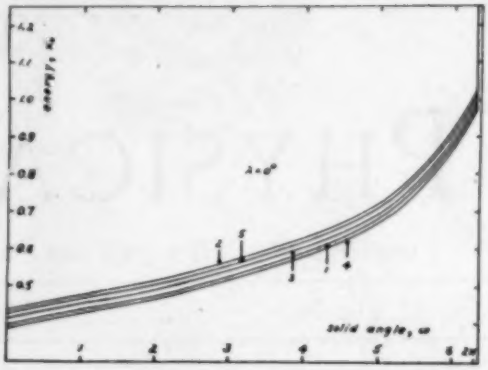

FIG. 2. The solid angle of opening of cone at several points on geomagnetic equator.

expect different intensities at different longitudes and consequently a longitude effect. We now show not only that this asymmetry of the earth's magnetic field is fully competent to account for the observations of Clay, van Alphen and Hooft, and of Millikan and Neher, but also that their intensity measurements along the geomagnetic equator throw valuable light on the energy distribution function of magnetically deflectable particles which give rise to both the latitude and the azimuthal effects.

In Fig. 1 the solid angle cut off from the unit sphere (i.e., the sky) by the allowed cone is plotted as a function of energy, measured in terms of our energy parameter[6] $x_0$, for geomagnetic latitudes 0°, 10° and 20°. The solid angle in each instance has been obtained by graphical integration from the calculations of Bouckaert.[7] In Table I we collect the results of a calculation of the distance from the earth's magnetic center to several points on its surface, together with the fractional change from the standard value of the energy parameter due to the fractional change in distance from the standard earth's radius (6370 km).

TABLE I. *Calculated distances from the earth's magnetic center to several points on its surface.*

| POINT NO. | GEOMAG. LAT. | GEOGR. LAT. | GEOGR. LONG. | DIST. (KM) | $\Delta x/x_0$ | APPROXIMATE LOCATION |
|---|---|---|---|---|---|---|
| 1 | 0 | 12 S | 76 W | 6519 | 0.0234 | Lima, Peru |
| 2 | 0 | 0 | 160 W | 6120 | −0.0393 | SS route Honolulu to Sydney or Melbourne |
| 3 | 0 | 10 N | 75 E | 6390 | 0.0031 | SS route Bombay to Colombo |
| 4 | 0 | 6 S | 15 W | 6650 | 0.0440 | SS route Southampton to Cape Town |
| 5 | 0 | 12 N | 110 E | 6220 | −0.0236 | SS route Hong Kong to Singapore |
| 6 | 0 | 10 S | 100 W | 6370 | 0 | 1000 miles SW of Galapagos |
| 7 | −10 | 2 N | 104 E | 6240 | −0.0204 | Singapore |
| 8 | 10 | 2 S | 80 W | 6520 | 0.0236 | Guayaquil |
| 9 | −20 | 6 S | 106 E | 6220 | −0.0236 | Batavia |
| 10 | 20 | 9 N | 79 W | 6460 | 0.0141 | Panama |

From the value of $\Delta x/x_0$ given in this table and from Fig. 1 one easily finds the solid angle of the cone (the full light region in the language of previous papers) for the different points in the table. The solid angle is plotted as a function of energy, expressed in terms of our energy parameter, for these points, in Figs. 2, 4 and 5.

Referring to Fig. 2 it is seen that for any given energy the full light region at the geomagnetic equator is greatest along curve 4 (for the point on the earth where the steamer lane from Southampton to Cape Town intersects the geomagnetic equator, approximately), is less for the same energy along curve 1 (Lima, Peru, approximately), then less along curve 3 (where the steamer lane from Bombay to Colombo intersects the geomagnetic equator), curve 5 (steamer lane from Hong Kong to Singapore) and least along curve 2 (steamer lane from

[6] G. Lemaitre and M. S. Vallarta, Phys. Rev. **43**, 89 (1933), Eq. (12). This amounts to choosing as our energy unit $1/10.60$ ergs, or $5.96\times10^{10}$ electron volts, for electrons or positrons.

[7] L. Bouckaert, Ann. de la Soc. Sci. de Bruxelles, **A54**, 174 (1934). Along the equator the angle of opening of the cone in the east-west vertical plane may be calculated from Störmer's formula $\sin\theta=-2\gamma_1/x\cos\lambda+\cos\lambda/x^2$ with $\lambda=0$ and $\gamma_1=1$, because there the vertex of the cone touches Störmer's circular cone as defined by the above expression. The angle of opening of the cone in the east-west vertical plane may *not* be calculated by this formula for any other latitude, since for no other latitude does this condition hold, nor may the solid angle of opening of the cone be calculated from this formula for any latitude including the equator.

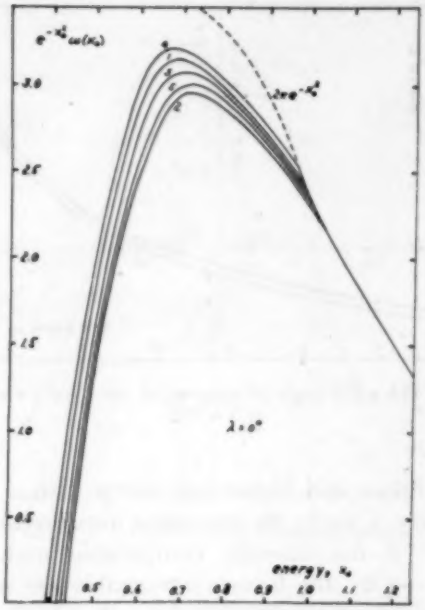


FIG. 3. The function $e^{-x_0^2}\omega(x_0)$ for different points on geomagnetic equator.

Honolulu to Melbourne). Consequently the total intensity must decrease in the same order.

We now calculate the percentage change in total intensity due to the fractional change $\Delta x/x_0$ in the energy parameter $x_0$, and show that the experimental results are consistent with the assumption that the energy distribution function, defined as the number of particles outside the atmosphere having a given energy, is an exponentially decreasing function of the energy. Let $f(x_0)$ be the distribution function and $\omega(x_0)$ the function giving the solid angle of the cone in terms of $x_0$. Then the number of particles coming through the cone corresponding to any particular value of the energy is, by Liouville's theorem,[8] $f(x_0)\omega(x_0)$. We now define the total intensity as the total number of particles which come through all the cones, beginning with those particles which have the least possible energy to reach the top of the atmosphere at the given point. This total intensity is given by

$$I=\int_{\bar{x}_0}^{\infty} f(x_0)\omega(x_0)dx_0.$$

[8] A discussion of the application of Liouville's theorem to the present theory, with full literature references, is given in reference 3.

Let us now assume that the distribution function is an exponentially decreasing function of energy. Remembering that for energies of the order of magnitude required to reach the tropical belt the energy is proportional to the square of the parameter $x_0$, we have for the total intensity,

$$I=\int_{\bar{x}_0}^{\infty} e^{-x_0^2}\omega(x_0)dx_0.$$

In Fig. 3 we have plotted as a function of $x_0$ the integrand of the above expression for the points in the geomagnetic equator given in our Table I. From this we have calculated by graphical and analytical integration the intensity $I_0$ at those points on the geomagnetic equator the distance of which from the magnetic center is equal to the earth's radius, i.e., the value of the above integral along curve 6 (or 3). This we have taken as our standard intensity with respect to which the percentage change of intensity due to the longitude effect is calculated. To find the change of intensity at the different points in our Table I we merely have to find by graphical integration the areas of the strips between corresponding curves in Fig. 3. For points 1, 2, 3 or 6, 4 and 5, respectively, we thus obtain $\Delta I_0/I_0=1.9$ percent, $-3.7$ percent, 0, 4.2 percent and $-2.5$ percent, respectively. The value of $\Delta I_0/I_0$ is different for the same $|\Delta x/x_0|$ because the areas of the corresponding strips are different.

Similarly for points 7 and 8 at $\lambda=\pm 10°$ the theory demands that the total intensity at the point on the earth described by curve 8 be greater than that described by curve 7 (Fig. 4) and the same calculation outlined above for equatorial points, with the same distribution function gives 5.6 percent as the percentage intensity change $\Delta I_1/I_1$ between these points. Likewise for points 9 and 10 (Fig. 5) at $\lambda=\pm 20$ the theory requires that the intensity at point 9 be less than that at 10, and a similar calculation gives for the percentage intensity difference $\Delta I_1/I_1=4.0$ percent.

We now proceed to compare our theoretical results with experiment. It is very fortunate that the steamer lane from Bombay to Colombo intersects the geomagnetic equator at a point, the distance of which from the magnetic center

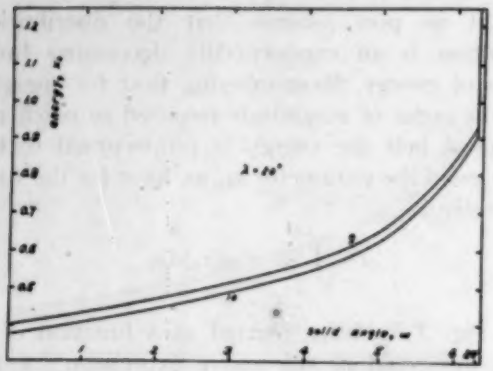

FIG. 4. The solid angle of opening of cone for two points at $\lambda = 10°$.

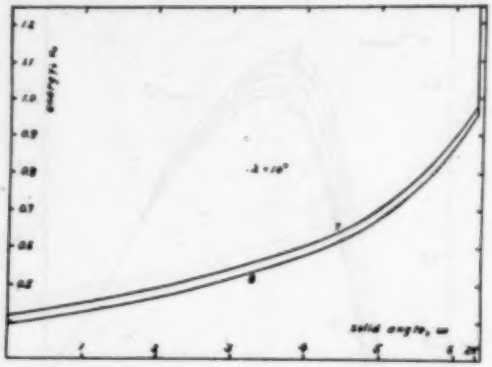

FIG. 5. The solid angle of opening of cone for two points at $\lambda = 20°$.

is very nearly the standard earth's radius. Consequently we have taken 1.73 as our standard ionization from which to reckon the intensity changes due to the longitude effect along the geomagnetic equator in the case of Clay, van Alphen and Hooft's measurements. Conditions are not so favorable in the case of Millikan and Neher's measurements because unfortunately they have not reported separately their measurements on the run from Hong Kong to Singapore and from Colombo to Bombay. However, the other point (point 6 in our Table I) which enjoys the same property of being at a distance from the magnetic center equal to the earth's radius is between Lima and the point where the steamer lane from Honolulu to Sydney intersects the geomagnetic equator. By interpolation we have taken as standard ionization in the case of Millikan and Neher's measurements the value 2.60 and have referred the percentage change of intensity due to the longitude effect to this value.

To compare the experimental value of the intensities at Guayaquil and Singapore we multiply the intensities given as ordinates in Millikan and Neher's[2] Fig. 2 by the factor 0.1191 so as to bring their high latitude values in their Fig. 2 into agreement with their high latitude values in their Fig. 5. This gives at Singapore the ionization 2.51 which is 5.2 percent less than the ionization at Guayaquil (2.64).

If one now desires to compare the intensity at Batavia as measured by Clay, van Alphen and Hooft with the intensity at Panama as measured by Millikan and Neher one meets with a grave difficulty. Clearly the ionization measured by the former is not directly comparable with that measured by the latter, presumably because of differences of construction in their respective apparatuses. If one attempts to reduce the former's values to the latter's by multiplying by the factor (1.374) which is required to make the high latitude value of the former agree with that of the latter one obtains the value 2.45 at Batavia which gives about 8 percent less intensity there than at Panama, where according to the latter the ionization is 2.64. If one attempts the reduction by multiplying by the factor (1.395) which is needed to make the former's measurements at Singapore agree with the latter's at the same point one obtains 2.47 as the ionization at Batavia, which is about 7 percent less than at Panama. It would appear that the conversion factor, besides depending on the apparatus, also depends on latitude. Further clarification of this point from the experimental side is earnestly to be hoped for.

The calculated and experimental results are compared in Table II, and the calculated longi-

TABLE II. *Calculated and observed values of* $\Delta I_1/I_1$ *and* $\Delta I_1/I_1$.

| POINT NO. | $\Delta I_0/I_0$ CALC. | $\Delta I_0/I_0$ OBS. | $\Delta I_1/I_1$ CALC. | $\Delta I_1/I_1$ OBS. | OBSERVERS |
|---|---|---|---|---|---|
| 1 | 1.9 | 1.2 | — | — | Millikan and Neher |
| 2 | −3.7 | −0.8 | — | — | " " |
| 3 | 0 | 0 | — | — | Clay, van Alphen and Hooft |
| 4 | 4.2 | 4.2 | — | — | " " " " " |
| 5 | −2.5 | −3.8(?) | — | — | Millikan and Neher |
| 7 | — | — | −5.4 | −5.2 | " " " |
| 8 | — | — | | | " " " |
| 9 | — | — | −4.0 | −7.0(?) | Clay, van Alphen and Hooft |
| 10 | — | — | | | Millikan and Neher |

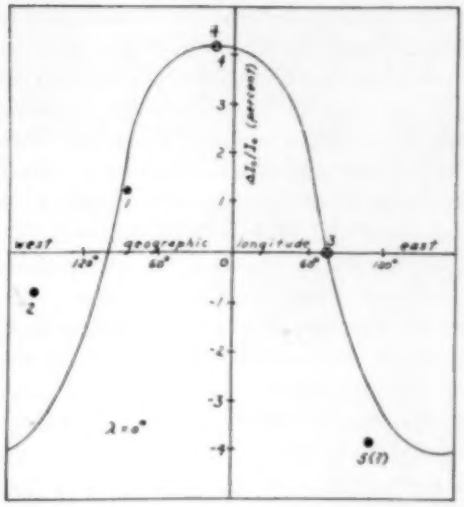


FIG. 6. The longitude effect along the geomagnetic equator.

tude effect at the geomagnetic equator is plotted in Fig. 6 together with the experimental points. The curve is symmetrical about the longitude 12 W approximately, but asymmetrical with respect to the axis of the abscissae.

With the exception of point 2 (SS route Honolulu to Melbourne at geomagnetic equator) it is seen that the agreement is very satisfactory.

The influence of atmospheric absorption will be considered in a future paper, but even without taking this factor into account it is seen from the above discussion that the theory is sufficiently in agreement with experiment. An additional factor which may affect the longitude effect is the bulging of the earth's atmosphere along the geographic equator due to the earth's rotation. Estimates of the magnitude of this effect are difficult to give at the present time, but in general it is clear that absorption would be greatest along the geographic equator and least at the poles. It is possible that the intensity at Lima may be affected by one percent due to this factor, as compared with the intensity at the west coast of Africa (SS lane Southampton to Cape Town at geomagnetic equator, point 4) but there seems to be no hope of accounting in this way for the high intensity measured by Millikan and Neher on the run from Honolulu to Melbourne, for there magnetic and absorption effects cooperate to give the least intensity.

We conclude that the theory of the latitude and azimuthal effects developed by Lemaitre and Vallarta is competent to account quantitatively for the longitude effect, and further that if the energy distribution function of the cosmic radiation which is responsible for these effects is substantially an exponentially decreasing function of the energy, the theory agrees with the measurements of the longitude effect.

My thanks are due to Dr. L. Bouckaert and Mr. E. J. Schremp who have helped me with the graphical integrations and with the discussion of the distribution function suggested in this paper.

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MAY 1, 1935 PHYSICAL REVIEW VOLUME 47

## Difference Bands in the Spectra of the Major Planets

ARTHUR ADEL AND V. M. SLIPHER, *University of Michigan and Lowell Observatory*

(Received March 11, 1935)

This brief paper contains the first identifications of difference bands in planetary spectra. These absorption bands lie at 816$\mu\mu$, 802$\mu\mu$, 683$\mu\mu$, 673$\mu\mu$ and 584$\mu\mu$. They are due to methane gas and are found in the spectra of Jupiter, Saturn, Uranus and Neptune.

IT is now well established that the atmospheres of the giant planets (Jupiter, Saturn, Uranus, Neptune) contain vast amounts of methane ($CH_4$) in a large excess of hydrogen, and that in the two former ones there is also present a relatively small amount of ammonia ($NH_3$).[1]

[1] A. Adel and V. M. Slipher, Phys. Rev. **46**, 902 (1934); H. N. Russell, Science **81**, 1 (1935).

The temperatures[1] which prevail in these atmospheres are all well below $-100°$C, so that the percentage of molecules occupying excited vibrational states is indeed small. The overwhelming molecular population residing in the ground state can be appreciated from the following simple example. The ratio of the number of methane molecules excited thermally to the mode of vibration $\nu_2 = 1520$ cm$^{-1}$, to the number of methane molecules in the ground state is very nearly given by $2e^{-h\nu_2/kT}$, the factor two being present in virtue of the isotropic nature of $\nu_2$ in two dimensions. In the Jovian atmosphere, above the clouds, where $T \leqq 163$, this ratio becomes $\sim 2e^{-13} = 1/200{,}000$; that is, about five molecules in every million are thermally excited to the $\nu_2$ fundamental vibration.

Despite the small percentage population resident in excited states, the actual number of thermally excited molecules appears to be sufficient to render certain of these levels apparent in absorption. Consider, for example, the absorption band at $683\mu\mu$[2] which appears in the major planet spectrum. We have observed it also in the laboratory, leaving no doubt that it is due to the methane molecule. In structure it is very narrow, contrasting markedly with the broad regions occupied by most of the thirty-six planetary methane bands already identified as having arisen in transitions from the ground state.[1] The spectrum given below (Fig. 1) shows the $683\mu\mu$ band in the presence of several others. It was obtained in the laboratory with 2140 meter-atmospheres of $CH_4$, at 47.6 atmospheres and $T \leqq 293°$. The narrow nature of the $683\mu\mu$ band is what might be expected in a band arising in absorption from an excited state whose population is completely insufficient for the development of the $P$ and $R$ branches and only barely adequate to exhibit a trace of development in the $Q$ branch.[3] Further evidence in support of this view is obtained from the fact that no plausible combination of frequencies can be found which would trace this band to a transition from the ground state, whereas it is at once correlated as a difference band; namely, as due to the transition from $\nu_2$ to $6\nu_3$. This places the band $6\nu_3$ at 6187A in excellent agreement with observation.[1] Besides $6\nu_3 - \nu_2$ at $683\mu\mu$, there appears also in the spectrum of Jupiter a structurally similar band at $816\mu\mu$.[4] In the same way, this band is to be identified as $5\nu_3 - \nu_2$. By way of description, we may say very briefly that $\nu_2$ is a symmetrical, double vibration, inactive in the infrared; and the sequence of bands $n\nu_3$ constitutes the strongest set in the major planet spectrum.

When we come to consider the probable appearance in the planetary spectra of other difference bands, it appears that just as $n\nu_3 + \nu_i$ gives rise to the strongest combination bands,[1] so the difference band sequence $n\nu_3 - \nu_i$ is the most likely to appear, in virtue of the great intensity of the set $n\nu_3$. $n$ is any integer, and $i$, of course, may be 1, 2 or 4.[5] We have already discussed

[2] V. M. Slipher, Lowell Observatory Bulletin No. 42.

[3] In virtue of the spherical symmetry of the methane molecule all of its absorption bands possess $P$, $Q$ and $R$ branches.

[4] V. M. Slipher, Pop. Astron. **37**, 140 (1929).

[5] The methane molecule possesses the four fundamental frequencies of vibration: $\nu_1 = 2915$, $\nu_2 = 1520$, $\nu_3 = 3014$, $\nu_4 = 1304$ cm$^{-1}$.

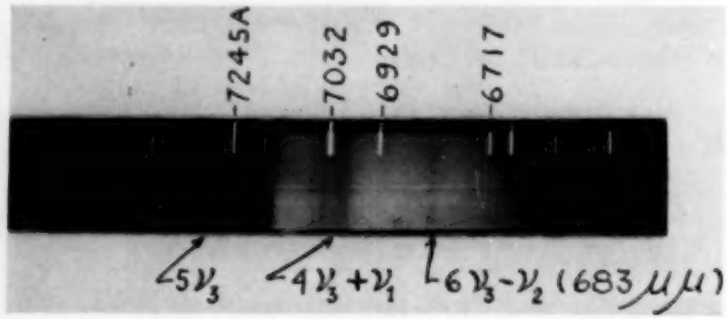


FIG. 1. Absorption spectrum of methane showing the $683\mu\mu$ band in the presence of several others.

the system $n\nu_3-\nu_2$; only the members $5\nu_3-\nu_2$ and $6\nu_3-\nu_2$ have been located. The system $n\nu_3-\nu_1$ may be expected to lie at approximately $921\mu\mu$, $754\mu\mu$, $644\mu\mu$ and $566\mu\mu$ for $n=5$, 6, 7 and 8, respectively.[6] $7\nu_3-\nu_1$ and $8\nu_3-\nu_1$ cannot be located in the spectra of the major planets. However, the spectra of Neptune and Uranus, where the bands $5\nu_3-\nu_1$ and $6\nu_3-\nu_1$ are most likely to be discovered, are unknown in this region.

We come finally to the group of bands $5\nu_3-\nu_4$, $6\nu_3-\nu_4$, $7\nu_3-\nu_4$ and $8\nu_3-\nu_4$, which may be expected to lie approximately at $802\mu\mu$, $673\mu\mu$, $584\mu\mu$ and $519\mu\mu$, respectively. The band $5\nu_3-\nu_4$ at $802\mu\mu$ is very prominent in the spectrum of Jupiter. In Uranus and Neptune, $6\nu_3-\nu_4$ is hidden by the mass of absorption $5\nu_3+\nu_1$,[2] while $7\nu_3-\nu_4$ is definitely present at $584\mu\mu$.[7]

It is evident that $n\nu_3-\nu_4$ is the strongest sequence with bands observable out to $n=7$: $n\nu_3-\nu_2$ is second, with $n$ reaching to 6; while $n\nu_3-\nu_1$ is very weak and, thus far, completely unobserved in the planetary spectrum.[8]

The allocation of observed difference bands relative to the several planets is given in Fig. 2.

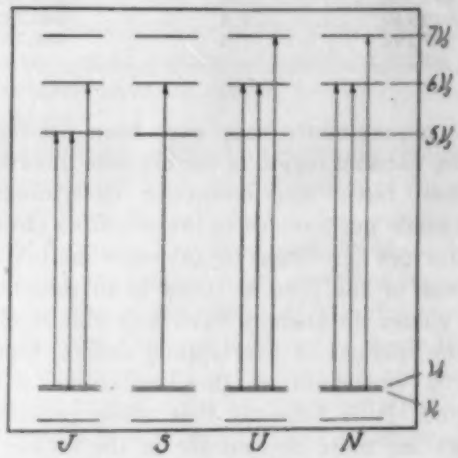


FIG. 2. Allocation of observed difference bands relative to the several planets.

[6] The absorption bands 5, 6, 7 and 8$\nu_3$ are centered at approximately $726\mu\mu$, $619\mu\mu$, $543\mu\mu$ and $486\mu\mu$, respectively.
[7] V. M. Slipher, Lowell Observatory Bulletin No. 13.

[8] The correlation of these five difference bands brings the total of identified methane bands in the major planet spectrum to forty-one.[1]

MAY 1, 1935 PHYSICAL REVIEW VOLUME 47

# Provisional Wavelength Standards for the Extreme Ultraviolet

J. C. BOYCE AND C. A. RIEKE, *George Eastman Research Laboratory of Physics, Massachusetts Institute of Technology*

(Received March 7, 1935)

This paper discusses the criteria for suitable wavelength standards in the extreme ultraviolet, and presents provisional values (obtained with a two-meter focus normal incidence vacuum spectrograph) for a number of lines of C, N, O and A falling in the spectral range between λ1850 and λ800. These are compared with the previous results of Edlén and of Bowen and of Bowen and Ingram. Further independent determinations are desirable. The present values, as those obtained by previous investigators, may be subject to a small systematic error inherent in the method of overlapping orders. This source of error is believed to be small, but must be eliminated before permanent standards can be established.

THE report of the commission on standards of wavelength of the International Astronomical Union contains the following criteria for auxiliary standards: "It is recommended that the mean wavelengths of the lines in certain groups of lines which give high orders of interference, and are satisfactorily distributed in the spectrum, and have been referred to the primary standard by three observers whose measurements are in satisfactory agreement, be adopted as working standards."[1] Tertiary standards are further defined as those obtained by interpolation between these secondary standards. It is well known that no standards which come anywhere near meeting

[1] Trans. Int. Astron. Union 1, 35 (1922).

TABLE I. *Hydrogen.*

| λ Observed | Wt. | λ Computed[2] |
|---|---|---|
| 1215.666 | 23* | 1215.664 |
| 1025.725 | 9 | 1025.717 |
| 972.538 | 6 | 972.532 |
| 949.740 | 4 | 949.739 |
| 937.792 | 1 | 937.799 |

TABLE II. *Helium* (He II).

| λ Computed[2] | λ Computed[2] |
|---|---|
| 303.7788 | 1640.409 |
| 256.3145 | 1215.129 |
| 243.0244 | 1084.940 |
| 237.3297 | 1025.270 |
| 234.3452 | 992.361 |
| | 972.109 |
| | 958.696 |
| | 949.326 |

these requirements have ever been established for the vacuum region of the extreme ultraviolet. Neither have interferometric determinations been made nor have three investigators obtained satisfactory agreement by any other method. The purpose of the present paper is to present the best values the authors have been able to obtain by the method of overlapping orders, together with a statement of the limitations of that method. It is believed that these preliminary values are more dependable in the region they cover than any previously published. It is hoped that independent work in this laboratory and elsewhere will soon confirm or revise them, and that in the interim they will be of use.

Comparison spectra in this region of the spectrum are most conveniently introduced by some form of gas discharge or by the presence of gases driven out by spark electrodes. Working standards should therefore be sought among the more common elements easily excited in a gas discharge, namely H, He, C, N, O, Ne and A. Lines of these light elements may not be so sharp as those of metals; nevertheless their widths are less than the available resolution of most vacuum spectrographs. For special purposes another set, such as the lines of Cu II, would be desirable. The present discussion wil be restricted to lines of these lighter elements.

Helium I and the various stages of ionization of neon are omitted, as their principal lines lie at shorter wavelengths than are considered here. While not literally satisfying the criteria quoted, the wavelengths calculated by Paschen[2] for the Lyman series of hydrogen and for the two series of ionized helium rest on a sound theoretical foundation and appear to be by far the most reliable in this region of the spectrum. For convenience these values (for a few of the strongest lines of each series) have been included in Tables I and II. The spectral range covered by these lines is limited, and their higher series members, particularly those of helium, are hard to excite.

Comparisons of these wavelengths have been made with values published by Edlén[3] and by Bowen[4] and by Bowen and Ingram.[5] The average difference between the wavelengths of Bowen and of Bowen and Ingram and the present preliminary standards is not more than a few thousandths of an Angstrom unit, though the individual values differ considerably, especially above λ1500 (here their wavelengths are usually given to only 0.01A). There is a good comparison with Edlén's standard lines only between λ800 and λ1200. The difference is constant and around 0.005A from λ800 to λ1050; it then increases to about 0.017A at λ1200. Below λ800, where we have compared with additional lines given by Edlén, we find the systematic difference to be less than 0.005A. We have made some use of Edlén's values, corrected for this systematic difference, below λ800 in drawing our reduction curves for neon and argon. The present article will therefore be restricted to the region from λ800 to λ1850. Adequate standards over such a range are urgently needed. When there is opportunity to obtain further independent measurements in the region of shorter wavelength they will be published, since it is important that Edlén's results obtained at grazing incidence be checked at more nearly normal incidence.

The standards of Bowen and Bowen and In-

[2] F. Paschen, Preuss. Akad. (1929), 662. See also W. G. Penney, Phil. Mag. **9**, 661 (1930).

[3] B. Edlén, Nova Acta Reg. Soc. Sci. Upsaliensis, Ser. IV **9**, No. 6 (1934), and Zeits. f. Physik **85**, 85 (1933).

[4] I. S. Bowen, Phys. Rev. **29**, 231 (1927).

[5] I. S. Bowen and S. B. Ingram, Phys. Rev. **28**, 444 (1926).

gram, those of Edlén, and the provisional values proposed in the present paper, were all obtained by a comparison, direct or indirect, of high orders of the lines in question with first orders of the secondary and tertiary standards obtained from an iron arc. They are all subject to the possible error inherent in the use of overlapping orders. This source of error has been investigated by Michelson[6] and by Kayser.[7] The amount of the error varies greatly with the imperfections of the grating used. It is also very sensitive to focal adjustment, and a grating in which this error is known to be small may suddenly develop a large error of this type if its adjustment is even slightly disturbed. The plates used in the present investigation are believed to be reasonably free of this type of error, to perhaps 0.005 to 0.010A. This belief is based upon a set of intercomparisons between different series of orders and upon the good agreement obtained with some of the wavelengths of H calculated by Paschen.[2]

The instrument used in this investigation was the two-meter normal incidence broad range vacuum spectrograph of the Carnegie Institution of Washington, which is located in the spectroscopy laboratory of the Massachusetts Institute of Technology. It has already been described in a paper,[8] which discusses the method of reduction of its plates. Results with neon have been published;[9] these depend to some extent on Edlén's wavelengths below λ800. For the wavelengths given in the accompanying tables, twelve exposures on five plates have been measured against the iron arc in the region λ2250 to λ2540, and three long exposures (on neon, argon and krypton plates) have been measured over their entire range. For the argon standards two additional exposures on argon were reduced, using the preliminary standards for C, N and O, which occurred as impurities in these exposures. Each plate was measured independently in both directions by two observers. The iron comparisons provide standards for those lines whose higher orders fall in this region of the plate. The reduction curves for other regions were drawn using as standards these lines and their intermediate orders, and on the krypton plate, lines of Kr II computed using the combination principle.[10] In addition the various orders of a given line were intercompared, and a few corrections were applied to those sections of the plate which had a relatively small number of standards. The three plates used have, of course, been reduced independently.

The probable error of a single observation has been computed from the differences of the measures on lines in their first order, according to Peters' formula. The lines used are those in the accompanying tables—all of shorter wavelengths than the iron comparisons. Hence the probable error includes the error in drawing the reduction curves in the regions where iron was not directly available; it is slightly less than ±0.007A for an observation of unit weight (one measurement in the first order). No considerable sources of systematic error suggest themselves with the exception of an error in the mean value of the twelve iron comparisons, and the possible error arising from the method of overlapping orders. The first of these might arise if the light from the arc failed to fill the grating, or if slight temperature changes occurred during the long gas exposure. Due precautions were taken to reduce both these sources of error, and they are believed to be less than the accidental error. The probable error of a single iron comparison has been found from the differences between the twelve plates measured. It equals ±0.007A for a single comparison and hence ±0.002A for the mean. Those lines measured against iron on fewer than the twelve exposures have been corrected to the mean system. Obviously, the accidental error of a line measured in the second order is one-half that in the first, etc. Some close multiplets were suspected of being affected by photographic errors in their first orders; for these lines the adopted wavelength depends only on measures in higher orders. The weight assigned to a measured wavelength is the summation of the products, number of plates times order.

In Tables III to VI the adopted wavelengths are given, followed by the results of Bowen or of

[6] A. A. Michelson, Astrophys. J. **18**, 278 (1903).
[7] H. Kayser, Astrophys. J. **19**, 157 (1904); **20**, 327 (1904).
[8] K. T. Compton and J. C. Boyce, Rev. Sci. Inst. **5**, 218 (1934).
[9] J. C. Boyce, Phys. Rev. **46**, 378 (1934).
[10] T. L. de Bruin, C. J. Humphreys and W. F. Meggers, Bur. Standards J. Research **11**, 409 (1933).

TABLE III. *Carbon.*

| λ | Bowen | Edlén | Int. | Spectrum | Wt. |
|---|---|---|---|---|---|
| 1930.900 | | | 5 | I | 3 |
| 1760.818 | .85 | | 4 | II | 3 |
| 1760.412 | .44 | | 3 | II | 3 |
| 1658.126 | .13 | | 3 | I | 3 |
| 1657.916 | .92 | | 3 | I | 3 |
| 1657.380 | .37 | | 2 | I | 2 |
| 1657.005 | .01 | | 6 | I | 3 |
| 1656.280 | .27 | | 4 | I | 2 |
| (1561.42) | .381 | | 8 | I | |
| 1560.699 | .660 | | 5 | I | 3 |
| 1560.316 | .267 | | 4 | I | 3 |
| 1550.790 | .774 | | 10 | IV | 2 |
| 1548.214 | .189 | | 12 | IV | 2 |
| 1463.33 | | | 3 | I | 3 |
| 1335.71 | .705 | .684 | 40 | II | 3 |
| 1334.54 | .539 | .515 | 30 | II | 3 |
| (1329.58) | .583 | | 6 | I | |
| 1329.101 | .100 | | 5 | I | 2 |
| 1328.831 | .839 | | 4 | I | 3 |
| 1323.94 | | .916 | 15 | II | 2 |
| 1280.340 | | | 2 | I | 2 |
| 1277.550 | | | 4 | I | 3 |
| 1277.274 | | | 4 | I | 3 |
| 1261.560 | | | 1 | I | 3 |
| (1261.12) | | | 1 | I | |
| 1260.955 | | | 2 | I | 2 |
| 1247.387 | .391 | .368 | 7 | III | 3 |
| 1194.491 | | | 3 | I | 3 |
| (1194.08) | | | 1− | I | |
| 1193.243 | | | 3 | I | 3 |
| 1193.012 | | | 1 | I | 3 |
| 1176.370 | .359 | .351 | 10 | III | 20* |
| 1175.986 | .988 | .973 | 9 | III | 14* |
| 1175.716 | .711 | .700 | 15 | III | 18* |
| 1175.582 | .577 | | 5 | III | 16* |
| 1175.259 | .261 | .248 | 9 | III | 18* |
| 1174.934 | .922 | .916 | 10 | III | 18* |
| 1141.745 | | | 1 | II | 2 |
| 1141.623 | .61 | | 3 | II | 8* |
| 1139.343 | | | 3 | II | 4 |
| 1066.138 | | | 5 | II | 6 |
| 1065.895 | | | 7− | II | 9 |
| 1037.020 | .021 | .017 | 10 | II | 8 |
| 1036.332 | .336 | .330 | 9 | II | 5 |
| 1010.374 | .382 | .369 | 7 | II | 6 |
| 1010.092 | .090 | .074 | 5+ | II | 6 |
| 1009.862 | .870 | .854 | 5 | II | 6 |
| 977.020 | .031 | .026 | 30 | III | 6 |
| 945.566 | | | 3 | I | 3 |
| 945.336 | | | 2 | I | 3 |
| 945.193 | | | 1 | I | 3 |
| 904.482 | .472 | .468 | 8 | II | 9 |
| 904.144 | .133 | .134 | 8+ | II | 6 |
| 903.952 | .960 | .950 | 8− | II | 6 |
| 903.614 | .620 | .609 | 8 | II | 9 |
| 858.559 | .561 | .561 | 6 | II | 6 |
| 858.091 | .088 | .094 | 5 | II | 5 |

Bowen and Ingram, and those of Edlén. The intensity was estimated on an arbitrary scale. The state of ionization is denoted by a roman numeral, and the final column gives the weight assigned to the determination. The probable error of each wavelength is then ±0.007A divided by the square root of the weight. Lines which have been measured in their higher orders against iron are indicated by an asterisk; a few below λ800 have been included. Some members of multiplets are included for identification purposes, although on account of blending they are not considered suitable for standards; these are given to two decimals and placed in parentheses. A few other lines are given to two decimals because the measurements are somewhat uncertain because of their great intensity or close companions. The computed hydrogen values are reprinted here for convenience and with them are our observed values of those lines for comparison. The computed values seem to us to be the more fundamental and should be used as standards, though in practice the lines are unfortunately often so broad as to be unsuitable.

The provisional values given here should be checked by other investigators. A few preliminary results provided by Professor Harrison in the current program of the Massachusetts Institute of Technology 21-foot normal incidence vacuum spectrograph indicate good agreement. Both the 21-foot spectrograph and the broad range two-meter instrument have gratings ruled at The Johns Hopkins University. It is important that

TABLE IV. *Nitrogen.*

| λ | Bowen | Int. | Spectrum | Wt. |
|---|---|---|---|---|
| 1745.246 | .260 | 2 | I | 3 |
| 1742.734 | .740 | 3 | I | 2 |
| 1494.669 | | 4 | I | 3 |
| 1492.630 | | 5 | I | 3 |
| 1243.297 | | 3 | I | 8* |
| 1243.170 | | 4 | I | 7* |
| 1200.706 | .681 | 4 | I | 19* |
| 1200.220 | .200 | 5 | I | 22* |
| 1199.547 | .533 | 6 | I | 23* |
| 1134.980 | .987 | 7 | I | 13* |
| 1134.419 | .420 | 5+ | I | 13* |
| 1134.171 | .180 | 5 | I | 7* |
| (1085.74) | .701 | 10 | II | |
| 1085.546 | .540 | 7 | II | 4 |
| 1084.579 | .566 | 9 | II | 9 |
| 1083.991 | .983 | 7 | II | 9 |
| (991.58) | .571 | 10 | III | |
| 989.804 | .803 | 7 | III | 9 |
| 916.708 | .698 | 8 | II | 7 |
| (916.01) | .018 | 6 | II | |
| (915.96) | .963 | 5 | II | |
| 915.612 | .603 | 5 | II | 9 |
| 775.966 | | 6 | II | 9* |

TABLE V. *Oxygen.*

| λ | BOWEN | EDLÉN | INT. | SPECTRUM | WT. |
|---|---|---|---|---|---|
| 1306.038 | | | 9 | I | 3 |
| 1304.864 | | | 12 | I | 3 |
| 1302.192 | | | 12 | I | 2 |
| 1217.645 | | | 10 | I | 10* |
| 999.494 | | | 6 | I | 9 |
| 990.797 | | | 4 | I | 6 |
| 990.213 | | | 8 | I | 4 |
| 990.121 | | | 3 | I | 4 |
| 988.775 | | | 8 | I | 9 |
| (988.64) | | | 3 | I | |
| 935.183 | | | 4 | I | 3 |
| 898.956 | | | 2 | III | 3 |
| 835.293 | .288 | .292 | 7 | III | 18* |
| (835.10) | .094 | .096 | 5 | III | |
| 834.467 | .462 | .462 | 20 | II | 30* |
| 833.749 | .741 | .742 | 11 | III | 18* |
| 833.332 | .326 | .326 | 12 | II | 30* |
| (832.93) | .926 | .927 | 5 | III | |
| 832.762 | .756 | .754 | 8 | II | 30* |
| 796.667 | .665 | .661 | 9 | II | 9* |
| 617.060 | .064 | | 7 | II | 8* |
| 616.304 | .309 | | 9 | II | 8* |
| 600.585 | .583 | | 5 | II | 8* |
| 599.594 | .600 | .598 | 10 | III | 16* |
| 580.974 | .975 | | 7 | II | 8* |

TABLE VI. *Argon.*

| λ | INT. | SPECTRUM | WT. |
|---|---|---|---|
| 1066.660 | 9 | I | 9 |
| 1048.218 | 8 | I | 9 |
| 932.046 | 10 | II | 9 |
| (919.78) | 15 | II | |
| 887.404 | 10 | III | 9 |
| 883.179 | 9 | III | 9 |
| 879.622 | 8 | III | 9 |
| 878.728 | 11 | III | 9 |
| 875.534 | 9 | III | 9 |
| 871.099 | 10 | III | 9 |

these results be checked by another investigator having a grating ruled by another engine.

When half the criteria for standards of the International Astronomical Union are satisfied, namely, satisfactory agreement between the results of three different observers, there still remains the question of a more certain method of comparison with the primary standard, or at least with the present secondary standards. Two lines of approach suggest themselves to eliminate the difficulty of the possibility of systematic error due to the use of the method of overlapping orders. The first is most direct and involves the use of some form of interferometer in a vacuum. Experiments along this line, under the direction of Professor Harrison, are in progress at this laboratory. The second depends on the combination principle and was suggested by Professor Shenstone. In an as yet unpublished investigation, Shenstone has examined the extreme ultraviolet spectrum of copper as excited in a Schüler lamp. He finds that many of the lines of Cu II in this region are those with wavelengths which can be predicted with great accuracy from terms calculated by visible or near ultraviolet combinations. It is now proposed to make exposures with the Carnegie Institution vacuum spectrograph under conditions which will give from the same source these copper lines and some of the provisional standards suggested in the present article. Direct comparisons of lines in the same orders will then eliminate the possible error inherent in the present results.

The program of research with its two-meter vacuum spectrograph was made possible by a grant to Dr. K. T. Compton from the Carnegie Institution of Washington. Grateful acknowledgment is also made of a grant to one of the writers from the Permanent Science Fund of the American Academy of Arts and Sciences. We wish to thank Mr. D. H. Clewell for his careful assistance in some of the measurements. The subject of this paper has been under discussion for several years with a number of spectroscopists, all of whom are thanked for many helpful suggestions. It is a pleasure to thank particularly Dr. Compton, Professor G. R. Harrison and Professor A. G. Shenstone.

# The Pure Rotation Spectra of $NH_3$ and $ND_3$

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The pure rotation spectra of $NH_3$ and $ND_3$ have been measured in the spectral region from $40\mu$ to $170\mu$. Ten rotation lines of $NH_3$ corresponding to final $J$ values from 3 to 12 have been observed. These fall upon a curve given by $\nu = 19.880J - 0.00176J^3$. Thirteen lines of $ND_3$ corresponding to final $J$'s from 8 to 20 have been observed. These fall upon a curve given by $\nu = 10.26J - 0.00045J^3$.

THE pure rotation spectrum of $NH_3$ was first studied by Badger and Cartwright,[1] who located five lines which fitted the formula $\nu = 19.957J - 0.00508J^3$ with an average deviation of $\pm 0.173$ cm$^{-1}$. Using a spectrometer which had a very much larger resolution, Wright and Randall[2] measured the three lines corresponding to $J = 5$, 6 and 7, respectively, and made possible an accurate determination of the doublet width. This they found to be $1.33 \pm 0.03$ cm$^{-1}$. The centers of the three lines fell upon a curve given by the formula $\nu = 19.880J - 0.00176J^3$ with an average deviation of $\pm 0.02$ cm$^{-1}$. The accuracy of these results is further guaranteed by their extremely close agreement with combination differences from the accurately measured near infrared bands.

It was the purpose of the present investigation to try to extend the measurements on $NH_3$ both to longer and shorter wavelengths, and to make similar measurements for the $ND_3$ molecule. This has been done and the preliminary results reported in a short note.[3] In this present paper the experimental procedure and the final results are given.

Since it was desirable to be able to study as great a portion of the far infrared as possible a wire grating spectrometer was selected rather than one employing an echelette grating. The instrument used was recently described by the author[4] and proved to be quite satisfactory from $30\mu$ to $180\mu$. Its main features were a Welsbach mantle source, f-2 mirrors of 6-inch diameter, a wire grating having 25 lines to the cm so spaced as to eliminate the even ordered spectra, and a radiometer as a receiving device. In order to obtain pure radiation in the various regions of the spectrum a set of filters, such as those described in the paper just mentioned, was used. As usual the entire spectrometer was enclosed in a metal case, the inside of which could be dried with $P_2O_5$ in order to remove the water vapor from the air. In spite of this precaution, the energy spectrum contained very clear indications of the rotation spectrum of water vapor. The samples of the gases studied were contained in glass cells of 4 cm diameter which had windows either of 1 mm sheets of paraffin (melting point 68–72°C) or 0.5 mm crystal quartz. These cells were filled by allowing the gases to flow through them until a sufficient quantity of the air had been displaced by the gas to give the desired absorption. They were always used at atmospheric pressure, and ranged in length from 4 cm in the case of $NH_3$ to 1 cm for $ND_3$. Transmission measurements were made at each wavelength with the cell and a dummy cell alternately in the path of the radiation, using a 0.5 mm plate of NaCl as a shutter. The deflections finally obtained were of the order of several mm and so a great many readings were necessary for each point, at least 8 being taken at each setting. The individual values of the percent transmission at any given wavelength are believed to be accurate to about $\pm 2$ percent. The many other experimental difficulties which are encountered in this region of the spectrum have been discussed elsewhere, and so need not be mentioned here.

The degree of resolution, and therefore the accuracy of the wavelength determinations, is limited in most cases by the finite width of the

[1] R. M. Badger and C. H. Cartwright, Phys. Rev. **33**, 692 (1929).
[2] N. Wright and H. M. Randall, Phys. Rev. **44**, 391 (1933).
[3] R. Bowling Barnes, W. S. Benedict and C. M. Lewis, Phys. Rev. **45**, 347 (1934).
[4] R. Bowling Barnes, R. S. I. **5**, 237 (1934).

slits which must be used in order to obtain readable deflections. In these measurements, the slits actually used were as follows: from 30$\mu$ to 85$\mu$, 0.75 mm; from 85$\mu$ to 122$\mu$, 1.5 mm; from 122$\mu$ to 180$\mu$, 2.0 mm. These represent "slit-widths" at 50, 100 and 150$\mu$ of 4.42, 1.67 and 1.14 $cm^{-1}$, respectively. In order to obtain as much resolution as possible readings were taken at intervals of $\frac{1}{3}$ of the slit-width. From the absorption lines of water vapor which were obtained in the background spectrum one sees that minima were located which are separated by about 1.0 $cm^{-1}$.

The spectrometer was not equipped with a divided circle. It would, however, have been possible to calculate the wavelengths from the geometrical arrangement of the instrument, but as there appeared to be very slight mechanical defects, manifested by small shifts in the measured position of the central image, a semi-empirical method of determining the calibration curve seemed preferable. This curve must have the form $\mu = a \sin (b \cdot \Delta l)$ where $\Delta l$ is the difference between the scale reading at the central image and at the wavelength $\mu$, and $a$ and $b$ are constants. In the measured energy and absorption curves, several lines appear at long wavelengths which can be accounted for only as lines of stated wavelengths appearing in the third order. For these lines $3 \sin (b \cdot \Delta l_I) = \sin (b \cdot \Delta l_{III})$, thus determining $b$. The three lines accurately measured by Wright and Randall; the neighboring $NH_3$ lines on either side, which should lie closely on their formula; and four strong lines of $H_2O$, whose calculated position is well known were now chosen as calibration points, and the best value of the constant $a$ found by fitting the curve to these points.

In Fig. 1 the rotation lines of $NH_3$ are shown, the ordinates giving the actual percent transmissions, no allowance having been made for the slight differences of absorption or selective reflection of the windows of the cell and dummy. These curves have been left as transmission curves purposely, in order to show clearly just exactly what has been measured. Particular attention is directed to the regions between the absorption lines, since they give a very good indication as to the spectral purity of the radiation used. Table I, which gives a summary of the results available on the far infrared of the $NH_3$ molecule, is self-explanatory. The calculated values of $\nu$ were obtained by using the formula of Wright and Randall given above. The observed values agree with the calculated $\nu$'s to $\pm 0.11$ $cm^{-1}$. As may be seen from the curves lines 3 to 6 show definite signs of being double. Line 3 falls in a region where part of the energy comes from overlapping third orders, and so the exact determination of its wavelength is difficult. The line at 152.35$\mu$ is the third order of line number 10 which occurs at 50.76$\mu$.

TABLE I. *The far infrared of $NH_3$.*

| Final $J$ | Obs. $\mu$ | Obs. $\nu$ | Calc. $\nu$ | Obs.[3] $\nu$ | Obs.[1] $\nu$ |
|---|---|---|---|---|---|
| 12 | 42.47 | 235.40 | 235.48 | | |
| 11 | 46.15 | 216.61 | 216.31 | | |
| 10 | 50.76 | 196.93 | 197.02 | | |
| 9 | 56.26 | 177.69 | 177.622 | | 176.10 |
| 8 | 63.14 | 158.33 | 158.129 | | 156.8 |
| 7 | 72.18 | 138.50 | 138.549 | 138.54 | |
| 6 | 84.07 | 118.92 | 118.896 | 118.90 | 118.60 |
| 5 | 100.78 | 99.20 | 99.178 | 99.180 | 99.06 |
| 4 | 126.04 | 79.32 | 79.406 | | 79.79 |
| 10/3 | 152.35 | 65.62 | 65.67 | | |
| 3 | 168.42 | 59.36 | 59.592 | | |

Samples of heavy ammonia, $ND_3$, were furnished us by Professor H. S. Taylor. These were prepared by reacting 99+ percent pure heavy water with magnesium nitride.[5] The resulting ammonia contained 97 percent D, as shown by ultraviolet absorption measurements. Fig. 2 shows again the actual transmission measurements. The simplicity of the spectrum found indicates that the absorbing gas in our cell was mostly

TABLE II. *The far infrared of $ND_3$.*

| Final $J$ | Obs. $\mu$ | Obs. $\nu$ | Calc. $\nu$ |
|---|---|---|---|
| 20 | 49.46 | 202.10 | 201.60 |
| 19 | 51.85 | 192.80 | 191.85 |
| 18 | 54.93 | 181.99 | 182.05 |
| 17 | 58.09 | 172.10 | 172.20 |
| 16 | 61.66 | 162.12 | 162.31 |
| 15 | 65.76 | 152.02 | 152.38 |
| 14 | 70.31 | 142.19 | 142.41 |
| 13 | 75.13 | 133.07 | 132.42 |
| 12 | 80.53 | 124.14 | 122.35 |
| 11 | 88.40 | 113.09 | 112.26 |
| 10 | 97.70 | 102.32 | 102.15 |
| 9 | 108.89 | 91.81 | 92.01 |
| 8 | 122.60 | 81.54 | 81.85 |

[5] H. S. Taylor and J. C. Jungers, J. Am. Chem. Soc. 55, 5057 (1933).

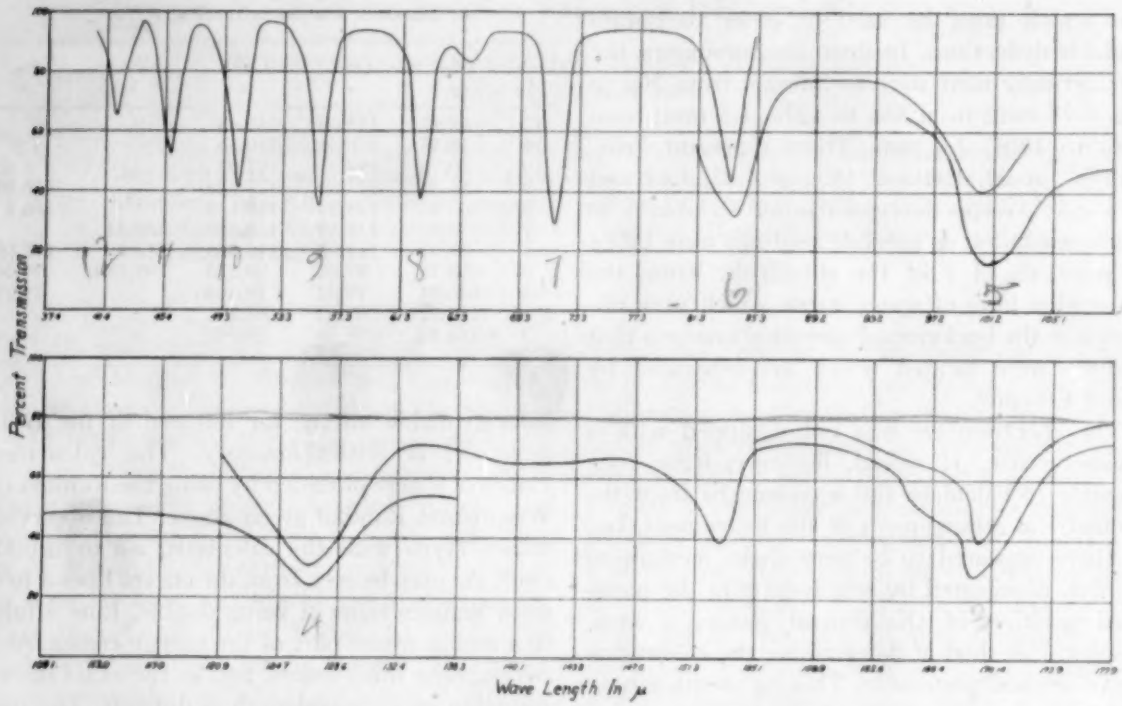


FIG. 1. Pure rotation spectrum of $NH_3$, showing absorption lines corresponding to final $J$ values from 3 to 12. The line at 152$\mu$ is a third order line. (The last numeral in each of the wavelength numbers is a decimal and should be preceded by a decimal point.)

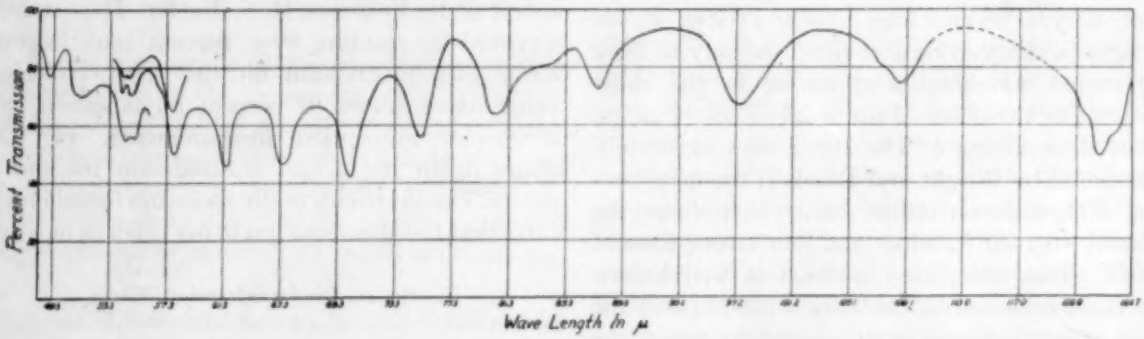


FIG. 2. Pure rotation spectrum of $ND_3$, showing absorption lines corresponding to final $J$ values from 8 to 20. (The last numeral in each of the wavelength numbers is a decimal and should be preceded by a decimal point.)

$ND_3$. A general background absorption (absent in the $NH_3$ curves), however, does suggest the presence of small percentages of unsymmetrical molecules such as $ND_2H$ and $NDH_2$. This is confirmed by ultraviolet measurements on the sample as used in our cell which indicated a purity of 85 percent D. Considering the crude method of filling the cells made necessary by the thin windows used, the presence of these impurities, due to exchange with atmospheric $H_2O$, is not at all surprising. Table II gives a summary of the $ND_3$ results. The calculated frequencies are given by the formula $\nu = 10.26J - 0.00045J^3$. It is seen that the agreement with observation, particularly in lines 11–13, is not good. This is undoubtedly due to the disturbing effect of the $NHD_2$ absorption, the background being particularly strong in this region. However, the question must be raised how accurately the simple formula, $\nu = 2BJ - 4DJ^3$ derived for linear molecules, is

FIG. 3. Schematic representation of the pure rotation spectra of $NH_3$ and $ND_3$. Intensities as shown are only approximate.

applicable to the symmetric rotator type. Dr. W. S. Benedict has shown that additional terms in the cubic formula are necessary, and are particularly important in $ND_3$. Since the present experimental results are not accurate enough to test this point, details will be reserved for a later time. For the present, the simple formula is taken, with $D_{ND_3}=\frac{1}{4}D_{NH_3}$; the resulting value of $B_{ND_3}=5.13$. From this and $B_{NH_3}=9.94$, the height of the pyramid may be calculated, since $1/B\sim I$ and

$$I_{NH_3}=(3/2)m_Ha^2+\frac{3m_Hm_N}{m_N+3m_H}q^2$$

and

$$I_{ND_3}=(3/2)m_Da^2+\frac{3m_Dm_N}{m_N+3m_D}q^2,$$

where $a$ is the distance from the symmetry axis to an H or D atom, and $q$ is the height. Solving, we find $q=0.36$A, $r_{N-H}=a^2+q^2=1.02$A. The accuracy of this result is not high, but the agreement with the value calculated indirectly, 0.37A, is good.[6]

Fig. 3 shows schematically the relative positions of the rotation lines of the two symmetrical ammonias.

The author wishes to express his appreciation to Drs. C. M. Lewis and W. S. Benedict who aided greatly in making these measurements, and to Professor Taylor and Dr. J. C. Jungers who prepared the heavy ammonia.

[6] Manning, J. Chem. Phys. 3, 136 (1935).

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# On Isotopic Shifts in the Spectra of Diatomic Molecules

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An inspection of the theory of diatomic molecules shows that the elementary theory of the dependence of the energy of diatomic molecules on the mass of the nuclei must be supplemented in two ways. In the first place the reaction of the nuclei to the precession of the electronic angular momentum about the internuclear axis gives a term

$$[B_e-\alpha(V+\tfrac{1}{2})][L(L+1)-\Lambda^2].$$

Furthermore there is a second positive term of uncertain magnitude. Both these terms are of importance only for very light molecules especially for the hydrogen molecule. The large electronic shifts observed for some band systems of $H_2$, HD and $D_2$ are well accounted for by this theory. A very accurate comparison of the constants of very light isotopic molecules necessitates also taking into account small corrections which appear in the higher order approximations of the energy values for a rotating anharmonic oscillator.

THE study of the spectra of molecules in which one or more of their atoms are substituted by the corresponding isotope can often furnish information about the structure of the molecule which cannot at all, or only with difficulty, be obtained in any other way. This is especially true for those molecules in which a hydrogen atom is replaced by its heavy isotope deuterium, because for this substitution the relative change in the masses is so much greater than for all other isotopic substitutions. In order to make full use of the material which can be obtained in this way it is necessary to know exactly the changes which must be expected in the structure of the corresponding energy levels and wave functions. The approximate theory which was hitherto quite adequate to give a satisfactory account of all the changes as long as only heavy atoms were concerned is not able to explain all the details for proton deuteron substitutions. Kronig[1] called attention to the fact that if certain terms in the Hamiltonian of a diatomic molecule which are usually omitted are taken into account, there is for many states a slight difference in the equilibrium distance even for the

[1] R. de L. Kronig, Physica 1, 617 (1934).

nonvibrating and nonrotating molecule. It is very difficult to prove such a difference experimentally, and it is very doubtful whether the effect discussed by Kronig is the cause for the discrepancies found by Holst and Hulthén[2] in the spectrum of AlH and AlD.

An investigation of the spectra of $H_2$, HD and $D_2$ must be expected to give the most detailed empirical information about the deviations from the elementary theory, as these deviations are all inversely proportional to the mass and therefore especially large for these light molecules. It is found that there are large electronic isotope shifts up to 25.6 $cm^{-1}$. The electronic isotope effect usually is understood to be the shift in the electronic frequency of a band system when one isotope is substituted for another. The electronic frequency is the frequency which the nonrotating and nonvibrating molecule would emit. It does not correspond to an actual line but can be obtained by extrapolation from the observed band lines of the system. In the following it is shown that shifts of this magnitude are demanded by theory. Furthermore, it is shown which terms have to be considered in order to find out a more accurate expression for the dependence on the molecular mass of the vibrational frequency and other constants.

## §1.

We shall restrict ourselves to the nonrotating molecule. The vibrational energy is then determined by

$$\left[\frac{h^2}{8\pi^2\mu r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)-V_e(r)+W^0\right]R(r)=0, \quad (1)$$

in which $R(r)$ is the vibrational eigenfunction and $V_e(r)$ the potential energy for fixed nuclei. If the electronic wave function for fixed nuclei is $\Phi$, the total wave function for the nonrotating molecule is

$$\psi=\Phi\cdot R. \quad (2)$$

(1) and (2) are valid only approximately, as certain terms of the complete Hamiltonian have been neglected.[3] We can introduce these terms now as perturbations with the perturbation function $H'$ such that

$$H'\psi=\frac{h^2}{8\pi^2\mu r^2}\left[(\mathbf{M}_\xi^2+\mathbf{M}_\eta^2)\Phi-r^2\frac{\partial^2\Phi}{\partial r^2}\right]R; \quad (3)$$

$\mathbf{M}_\xi$, $\mathbf{M}_\eta$, $\mathbf{M}_\zeta$ are the components of the orbital angular momentum[4] with respect to axes fixed to the molecule. (The $\zeta$ axis is the internuclear axis.) We shall consider in this paper only the first term in this expression. For an evaluation of the influence of the second term a knowledge of the $\Phi$ would be necessary. The empirical data seem to show that its influence for the two levels for which sufficiently accurate data are available is small compared to that of the first term.

The influence of (3) on the energy is in the first approximation

$$W_1'=\int\bar{\psi}H'\psi dv=\int\bar{R}Rdr\int\bar{\Phi}H'\Phi dv'. \quad (4)$$

We have

$$(\mathbf{M}_\xi^2+\mathbf{M}_\eta^2)\Phi=(\mathbf{M}^2-\mathbf{M}_\zeta^2)\Phi$$
$$=[L(L+1)-\Lambda^2]\Phi, \quad (5)$$

in which $\mathbf{M}$ is the operator corresponding to the total orbital momentum. $L$ is the quantum number corresponding to this operator and $\Lambda$ that corresponding to $\mathbf{M}\zeta$. (5) is correct only if the angular momentum is constant. This will be the case especially for higher levels of light molecules, but (5) can be expected to be a fairly good approximation also for most other molecular levels. The contribution of the first term in (3) to the energy is therefore, if we take for $r$ its equilibrium value, $B_e[L(L+1)-\Lambda^2]$. To obtain a better approximation, we remember that (4) means averaging over the electronic motion and the nuclear vibrations. The averaging over the electronic motion is taken care of by (5), whereas the averaging over the nuclear vibrations concerns only the quantity $B=h/8\pi^2\mu r^2$. This same average occurs when the rotational energy of a rotating oscillator is calculated and its value is

[2] W. Holst and E. Hulthén, Nature **133**, 496 (1934); Zeits. f. Physik **90**, 712 (1934).

[3] J. H. Van Vleck, Phys. Rev. **33**, 467 (1929). See also R. de L. Kronig, *Band Spectra and Molecular Structure*, Cambridge, 1930.

[4] We restrict ourselves then to singlet levels, as in general $\mathbf{M}$ is the *total* angular momentum. We can nevertheless apply the results obtained in this way to the triplet bands of hydrogen, as in this case the spin is so loosely coupled to the rest of the molecule that for all practical purposes the properties of the triplet levels are the same as those of singlet levels.

$B_e-\alpha(V+\frac{1}{2})+\cdots$. It is essential for this that the deviations from harmonic oscillations are taken into account, for otherwise $\alpha$ would have the same order of magnitude but opposite sign. The contribution of the first term in (3) to the energy is thus

$$W_1'=[B_e-\alpha(V+\tfrac{1}{2})][L(L+1)-\Lambda^2]. \quad (6)$$

The part independent of the vibrational quantum number $V$ would in the usual empirical analysis of the energy levels of a diatomic molecule be classed with the electronic energy. It differs however from it because it depends on the mass of the nuclei and does not occur in the energy of the molecule with fixed nuclei. Its physical significance is that it represents the reaction of the nuclei to the precession of the electronic angular momentum about the internuclear axis. (3) shows that it is proportional to the square of the component of the angular momentum perpendicular to the internuclear axis, and it is evident that this must be present also for the nonvibrating and nonrotating molecule. The magnitude of this term can be easily calculated as all the constants are known from the rotational and vibrational analysis of the corresponding bands. The term is zero only for $S\Sigma$ levels. As this and all other similar terms are proportional to $B$ it is evident that they are most significant for the hydrogen molecule because on account of the light masses of the hydrogen nuclei $B$ is so much larger than for any other molecule.

## §2.

### Comparison with Experimental Values

It is obvious that the constant part of (6) cannot be separated from the true electronic energy if only the $H_2$ levels were known, but if also the corresponding HD or $D_2$ levels are known the two parts can be determined separately. There are in the spectrum of the hydrogen molecule two levels which are analyzed with sufficient detail and accuracy to allow an experimental test of the above formula. These are the $3p^3\Pi$ level[5] for which $L=1$ and $\Lambda=1$ and the $3p^3\Sigma$ level[6] for which $L=1$ and $\Lambda=0$. The observed origins of the band systems corresponding to transitions from these two levels to $2s^3\Sigma$ are:

| | $H_2$ | HD | $D_2$ |
|---|---|---|---|
| $3p^3\Pi\rightarrow 2s^3\Sigma$ | 16,793.87 | 16,788.86 | 16,783.92 |
| $3p^3\Sigma\rightarrow 2s^3\Sigma$ | 11,838.91 | 11,825.68 | 11,813.40 |

The observed shifts and those calculated from (6) are:

| | $H_2-HD$ | | $HD-D_2$ | |
|---|---|---|---|---|
| | obs. | calc. | obs. | calc. |
| $3p^3\Pi\rightarrow 2s^3\Sigma$ | 5.01 | 7.55 | 4.94 | 7.61 |
| $3p^3\Sigma\rightarrow 2s^3\Sigma$ | 13.23 | 13.44 | 12.28 | 12.62 |

It is difficult to judge the accuracy of the observed origins. They must be obtained by extrapolation from many observed lines and there is always the danger of systematic errors of uncertain magnitude if the formula used is not a sufficiently good approximation. The uncertainty due to errors in the measurements is only a few hundredths of a wave number and it is estimated that the total uncertainty is not more than one wave number, probably much less. The only exception is perhaps the value for the origin of $3p^3\Sigma\rightarrow 2s^3\Sigma$ of $H_2$ for which Richardson's value was taken which was computed from less complete data, and may have therefore possibly a larger error.

It is seen that the general agreement between the empirical and theoretical values is very satisfactory, which shows that very probably the largest part of the observed shifts is given by (6). In particular the isotopic shifts have the right sign and the shift for the $p^3\Sigma$ levels is about twice that of the $p^3\Pi$ level as it should be.

As a rule there is no difficulty in finding the $\Lambda$ value for a given electronic level from the structure of the bands in question. To find the $L$ values is much more difficult and requires a much more complete knowledge of the whole spectrum. With the isotope effect discussed here it may be often possible to fix the $L$-values in cases of doubt.

The remaining discrepancies between the observed and calculated values may be partly due to the neglected second term in (3). This term must also be positive, but there is no reason why it should be zero for $s\Sigma$ states. It must be expected that its contribution will be larger for the lower states, so that the difference between the contribution of the initial and final state which

[5] G. H. Dieke and R. W. Blue, Phys. Rev. **47**, 261 (1935).
[6] G. H. Dieke, to appear shortly in Phys. Rev.

enters into the band origins will be negative. The corrections due to the second term in (3) have therefore the right sign to reduce the discrepancies between the above theoretical and observed values.

There are two other band systems of hydrogen for which at present there are sufficient data for a calculation of the electronic shifts. They are the ultraviolet band systems $2p^1\Pi \rightarrow 1s^1\Sigma$[7] and $2p^1\Sigma \rightarrow 1s^1\Sigma$.[8] The difference between the $H_2$ and HD origins of both systems has the opposite sign from that of the two visible systems. The values of the shifts are 8 $cm^{-1}$ for $2p^1\Pi \rightarrow 1s^1\Sigma$ and 12 $cm^{-1}$ for $2p^1\Pi \rightarrow 1s^1\Sigma$ with a probable error of about 5 to 10 $cm^{-1}$. If these values are correct it shows that the second term in (3) must be much larger for the normal state $1s^1\Sigma$ than for any excited state, so that it can compensate for the positive shifts due to the first term in (3) which are of the same order of magnitude as those found for the visible bands. Such an assumption does not seem altogether improbable.

For the lines of the hydrogen and deuterium atoms we find a shift due to the common motion of nucleus and electron about the center of gravity. It is 8.25 $cm^{-1}$ for $H\alpha$ and 44.5 $cm^{-1}$ for $L\alpha$, the line of the heavier atom having the higher frequency. Such an effect, because of the fact that the center of gravity of the nuclei and electrons do not coincide, is not taken into account in Van Vleck's treatment of diatomic molecules on which the foregoing considerations are based. It must be expected, however, to be much smaller for systems with more than one electron. The motion which the center of gravity of the nuclei executes because of the motion of one electron is at least partly counterbalanced by the motion of the second electron. Therefore the total effect will be much smaller. This is analogous to the fact that the energy level series of the helium atom are best represented with the Rydberg constant for an infinite mass and not with that for a mass four.

## §3.

## The Effect on the Vibrational Frequency

The term linear in $V+\frac{1}{2}$ of (6) has the effect that the frequency $\omega_e$ calculated according to (2) with $V_e(r)$ as potential must be diminished by $\alpha[L(L+1)-\Lambda^2]$ in order to obtain the total coefficient $\omega_e'$ of $V+\frac{1}{2}$ in the energy formula. $\omega_e'$ is the quantity which is determined empirically and usually designated as the vibrational frequency.

In going from one isotope to another $\omega_e$ varies with the first power of the transformation coefficient $\rho$, whereas $\alpha$ varies with the third power.[9] $\omega_e'$ which is the quantity empirically determined from the experimental data varies, therefore, not exactly with $\rho$ but should show slight variations. A rigorous experimental proof of this is at present not yet quite possible as the empirical values of the constants are not quite reliable enough. Table I shows the effect of this correction. This table is given with the intention to show how much these corrections affect the $\omega_e'$ ratios rather than to show the agreement with the calculated values of $\rho$ of the last row. The corrections of the next paragraph may be of the same order of magnitude, and it would be necessary to take them into account also if the comparison is intended to be of such a high degree of accuracy. It may be remarked, however, that the agreement between the observed and calculated values for $3p^3\Pi$ is of nearly the same order with and without the corrections. The $3p^3\Sigma$ state offers a better case as the corrections are about twice as big as those for the $3p^3\Pi$ state. The agreement in the first two columns is poor in any case. This is very probably because of a too low $\omega_e'$ value for $H_2$, which was calculated by Richardson and Das[10] from much scantier and less accurate empirical material. The last column shows, however, a much better agreement with the correction than without it.

Table I.

| | | HD : $H_2$ | $D_2$ : $H_2$ | $D_2$ : HD |
|---|---|---|---|---|
| $3p^3\Pi$ | without corr. | 0.86634 | 0.70764 | 0.81682 |
| | with $\alpha$ corr. | 0.86620 | 0.70741 | 0.81668 |
| $3p^3\Sigma$ | without corr. | 0.86751 | 0.70881 | 0.81706 |
| | with $\alpha$ corr. | 0.86722 | 0.70832 | 0.81676 |
| | calc. | 0.86616 | 0.70744 | 0.81675 |

[7] C. R. Jeppesen, Phys. Rev. **45**, 480 (1934).
[8] K. Mie, Zeits. f. Physik **91**, 475 (1934).
[9] This statement is subject to the corrections of § 4.
[10] O. W. Richardson and K. Das, Proc. Roy. Soc. **A125**, 309 (1929).

## §4.

### Corrections for the Energy Values of the Anharmonic Oscillator

The constants in the familiar expression,

$$\omega_e(V+\tfrac{1}{2})-x(V+\tfrac{1}{2})^2+y(V+\tfrac{1}{2})^3-z(V+\tfrac{1}{2})^4+\cdots$$

for the vibrational energy of an anharmonic oscillator are according to the elementary theory multiplied by the first, second, third and fourth power of $\rho$, respectively, in an isotopic substitution. This is true, however, only approximately and if one goes to higher approximations, correction terms have to be added which require a different power of $\rho$ as isotopic transformation factors. These corrections do not show in the formulae which Fues[11] first derived with the wave mechanics because he did not go to high enough approximations, but they are fully given in a treatment by Dunham.[12] If the potential energy is written

$$V(r)=a_0\delta^2[1+a_1\delta+a_2\delta^2+\cdots]$$

in which $\delta=(r-r_0)/r_0$; all the constants are supposed to be independent of the nuclear masses. The energy of a rotating oscillator having this potential can be written in the form

$$\sum_{l,\,k} Y_{lk}(V+\tfrac{1}{2})^l[J(J+1)]^k$$

and Dunham gives the first 15 of the coefficients $Y_{lk}$. A few examples are sufficient to show what kind of corrections appear. If $\beta=B_e/\omega_e$, we have

$$Y_{00}=(B_e/8)(3a_2-7a_1^2/4),$$

$$Y_{10}=\omega_e[1+(\beta^2/4)(25a_4-95a_1a_3/2-67a_2^2+459a_1^2a_2/8-1155a_1^4/64)],$$

$$Y_{01}=B_e[1+(\beta^2/2)(15+14a_1-9a_2+15a_3-23a_1a_2+21(a_1^2+a_1^3)/2],\ \text{etc.}$$

[11] F. Fues, Ann. d. Physik **80**, 367 (1926).
[12] J. L. Dunham, Phys. Rev. **41**, 721 (1932).

It is not the purpose of the present paper to give an accurate evaluation of these corrections,[13] but a few remarks may show of what order of magnitude they are.

Let us consider first the term $Y_{00}$ which can be considered as a correction to the electronic energy. It can be evaluated with ease if we make use of the approximate expressions

$$Y_{20}=-x=(3B_e/2)(a_2-5a_1^2/4),$$

$$Y_{11}=-\alpha=6B_e\beta(1+a_1).$$

It is sufficient to give the constants for $D_2$. They are

| | $\beta^{-1}$ | $a_1$ | $a_2$ | $Y_{00}$ |
|---|---|---|---|---|
| $2s^3\Sigma$ | 110.4 | −1.59 | 1.83 | 2.24 |
| $3p^3\Pi$ | 110.4 | −1.67 | 2.03 | 2.34 |
| $3p^3\Sigma$ | 113.1 | −1.70 | 1.95 | 1.34 |

For HD $Y_{00}$ is 1.5 times and for $H_2$ twice as big as for $D_2$, which means that the shift between $H_2$ and $D_2$ is just equal to the value of $Y_{00}$ for $D_2$ given in the table. The isotopic shift of the origin of the band systems which is the difference between the shifts of initial and final level is therefore +0.10 for $3p^3\Pi\rightarrow 2s^3\Sigma$ and −0.90 for $3p^3\Sigma\rightarrow 2s^3\Sigma$. These shifts, though of sufficient magnitude to be noticeable with accurate observations, are small compared with the effect discussed in §2, and will be in general altogether insignificant for heavier molecules.

The effect of these corrections on $\omega_e$ and $B_e$ may be of sufficient magnitude to change appreciably the empirical ratios of these constants for the different hydrogen isotopes and should therefore be taken into account, if an accurate test is made. This will be considered in a later paper.

[13] For a reliable calculation of the constants $a_1$, $a_2$, $a_3$ and $a_4$ which are all necessary for an evaluation of the correction for $\omega_e$ it would be necessary to know accurately some of the constants which occur only as small terms in the empirical expression of the energy. It would be a waste of time to attempt this unless the best available data can be used. As we are still improving constantly the empirical data for the three hydrogen molecules, we are postponing a detailed discussion of all these corrections to a later date.

# A Modified Aston-Type Mass Spectrometer and Some Preliminary Results

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A modified Aston-type mass spectrometer is described, in which ionization is produced by controlled electron bombardment. The electric field used is radial, and the shape of the magnetic pole faces was calculated to give the necessary velocity focusing. A special type of filament assembly is employed to minimize the energy spread of the emitted electrons. An amplifier circuit is described using a Western Electric D-96475 tube which gives high sensitivity combined with good stability. A new device is described for giving a continuous indication proportional to the square of the magnetic field. Some preliminary results are included on the ionization of $N_2$, CO, $NH_3$, $N_2H_4$.

IN order to obtain increased resolving power for the study of positive ions resulting from controlled electron bombardment, a modified Aston-type mass spectrometer has been constructed and some preliminary results will be given. The general arrangement is shown in Fig. 1. The gas to be investigated is admitted at $G$ into a capillary tube. The gas is released from the capillary at about the center of the filament assembly $F$ where it is bombarded by electrons accelerated radially inward. The resulting ions are then accelerated by a 1500-volt potential applied between $F$ and the anticathode $A$. $A$ is grounded through a microammeter to permit measurement of the positive ion current incident on it, which is used as an indication of the total current through the mass spectrometer. The collimator consists of two slits, $C$, 40 cm apart and each 2.5 mm × 0.1 mm. The collimated beam next passes through the electric deflecting field $E$ whose plates are equiangular sectors of coaxial cylinders, and in this field the beam is spread out into an energy spectrum. This divergent beam next enters the magnetic field $M$ whose leading and trailing edges were calculated to focus all particles of a given value of $e/m$ on the focal slit $S$, and any desired value of $e/m$ can be focused by suitable adjustment of the magnetic field strength. The leading and trailing edges of $M$ are slightly concave but no attempt has been made to indicate their true shape for the drawing is too small.

With the exception of necessary electrical insulation the apparatus is constructed of metal. The magnetic circuit is made of Rema dead soft electric furnace charcoal iron. The remainder of the apparatus is of brass, with gold slit jaws and gold plated deflecting plates. The plug of the large ground joint carrying the filament assembly is of Pyrex ground into a steel sleeve.

The path of a charged particle in the radial electric field was kindly obtained by Mr. G. C. Munro of this laboratory. Neglecting edge effects the field between the two plates is an inverse first power field. All the rays are assumed to be parallel and to enter the field at the same point, on the leading edge midway between the plates. It is required to find the emergent paths and velocities for the velocity determines the radius of curvature in the magnetic field and the emergent path determines the point of incidence in the field. The point of emergence of the ray on the trailing edge of the electric field, the emergent velocity, and the angle between the emergent ray and a reference ray were each determined in terms of one of three convergent infinite series in a parameter, $\kappa=\phi_0/2E \ln(\rho_2/\rho_1)$. $\phi_0$ is the voltage applied between the electric field plates of radius $\rho_2$ and $\rho_1$, and $E$ is the energy of the particle in electron volts. If the center of curvature of the plates is taken as the origin, a circle of radius $\alpha$ about this point passes through the point of incidence of the rays and the radius to the point of emergence of any ray is $\rho=u\alpha$. $u$ is described by $u=1+(1-\kappa)f(\kappa)$.

The tangent of the angle between the emergent ray and the reference ray is $(1-\kappa)F(\kappa)$. The relation between the emergent velocity $V$ and the incident velocity $v$ is $V^2=v^2[1-\kappa(1-\kappa)\phi(\kappa)]$.

A range of $\kappa$ from 0.7 to 1.3 covered the entire usable part of the field but the calculations

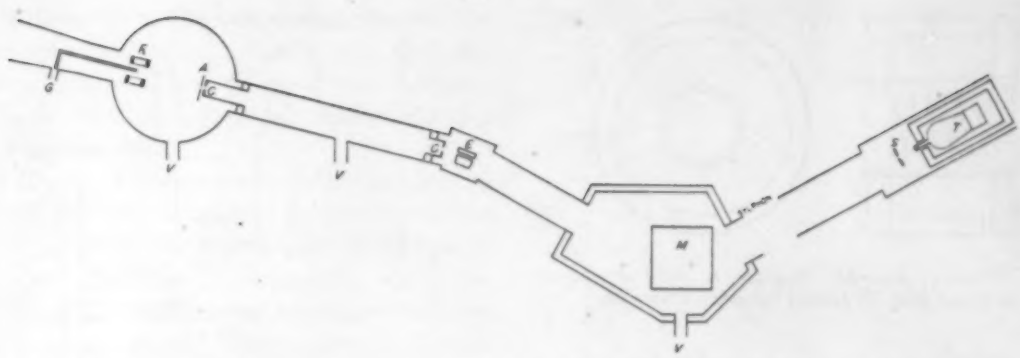

FIG. 1. Diagram of mass spectrometer. *G*, gas inlet to capillary; *F*, filament assembly—see Fig. 2; *A*, graphite anticathode; *C*, collimator slits; *E*, electric deflecting field; *M*, magnetic deflecting field; *S*, focal slit; *T*, Western Electric Co. D-96475 tube; *V*, vacuum pumping connections.

were extended from $\kappa = 0.5$ to 1.5. Since the analysis of the electric field disclosed no analytic expression for the characteristics of the beam after traversing the electric field, the only available method of determining the proper shape of the magnetic field lay in assigning appropriate values to the parameter $\kappa$ and then determining radius of curvature and point of incidence on the magnetic field for a sufficient number of rays. It was found that the calculation could be greatly simplified by introducing the further restriction on the magnetic field that it be symmetrical with respect to the bisector of the angle between the incident and emergent median rays. A total of fifty-five points was calculated on the leading edge of the magnetic field and then by means of a Schwartz transformation the edge effect was investigated and the points were corrected accordingly. The results of the edge effect calculation show that to a reasonable approximation the line integral of the magnetic field along the path of a particle is the same as if the uniform field were taken to extend beyond the edge a distance equal to eight-sevenths of the air gap.

An attempt was made to approximate the curve by means of an ellipse which could be generated on a milling machine, but no conic section gave a satisfactory fit.

The half-width of the iron at the bottom of the field is 1.789 inches, the minimum half-width is 1.768 at 1.600 inches above the bottom, and the half-width is 1.808 inches at a point 3.0 inches from the bottom, above which no rays enter.

A sylphon is introduced between the magnetic field and the focal slit to permit radial and tangential motion of the focal slit for adjustment of focus.

Unfortunately the theoretical work of R. Herzog[1] was not available when this apparatus was designed but it has since been applied. The electric deflecting field has a radius of curvature for the median ray of 12 cm and is equivalent to a cylindrical lens of 24.5 cm focal length plus a prism. The magnetic field has a radius of curvature of 10 cm for the median ray and is equivalent to a cylindrical lens of 11.9 cm focal length plus a prism. In both fields the intersection of the principal planes coincides with the intersection of the median rays. The first collimator slit has an inverted image 33.3 cm in front of the focal slit *S*, and the image of the second collimator slit is 23.8 cm in front of *S*. The width of image observed at *S* is consistent with that calculated from the positions and dimensions of their optically determined images.

Vacuum pump connections are provided at the three points marked *V*.

The filament assembly is shown in more detail in Fig. 2, and has proven quite satisfactory in most respects. The entire body is made of Acheson graphite and consists of two disks and a short cylinder attached to one of them. Eight helical tungsten filaments *F* are arranged as shown and no electrical connection to them is required other than a sliding fit in the holes drilled in the graphite. The grid *G* is

[1] R. Herzog, Zeits. f. Physik **89**, 457 (1934).

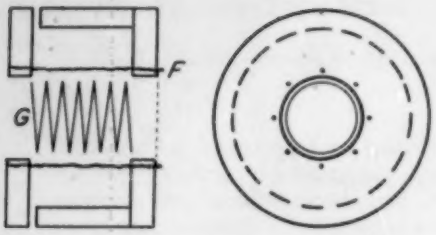


FIG. 2. Filament assembly diagram. *G*, helix of tungsten wire for grid; *F*, helical tungsten filaments.

also helical and is so proportioned that it withstands a potential drop equal to and in the same direction as that in the filaments, thus largely eliminating the variation in electron energy due to the filament drop. This also results in an axial field tending to draw the positive ions out of the filament assembly where they can be affected by the larger field applied between *F* and *A*. The chief disadvantage of this arrangement is the penetration of the larger field into the filament assembly so that as yet no check on ionization potentials is possible.

The amplifier circuit employed, as shown in Fig. 3, is notable chiefly for its simplicity for it has not been found necessary to modify the circuit for individual tube differences. The resistance values given were calculated only to give the recommended potentials and the behavior of the circuit has been most satisfactory from the start. The zero drift is consistently less than 2 cm per hour with a sensitivity of $10^{-17}$ amp./mm, and random fluctuation of 3–4 mm, which compares favorably with the various compensated circuits published up to this time. Two factors contribute to this stability. The first is the use of large batteries, 240 amp. hr. capacity, so that the voltage drift is negligible. The second is the careful shielding against thermal disturbances in addition to the necessary careful electrical shielding. All of the resistances in the circuit, excepting only the grid resistance of $10^{12}$ ohms, are immersed in transformer oil which effectively prevents temperature fluctuations. The number of variable contacts is reduced by soldering all possible contacts, leaving only those needed for adjusting filament current and galvanometer zero. Some trouble was caused by poor insulation resistance in the leads from the control box to the tube

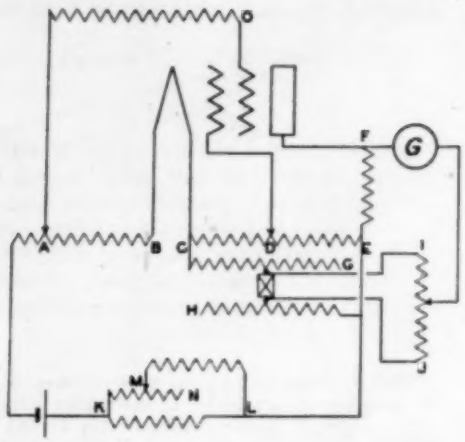


FIG. 3. Circuit diagram. Resistance $AO = 1.3 \times 10^{12}$; $AB = 11.1$; $CD = 12.25$; $DE = 8.65$; $EF = 25{,}000$; $CG = 200$; $EH = 200$ (dual); $IJ = 2$; $KL = 10$; $KN = 200$; $LM = 40$. Battery—12v, 240 amp. hours. Galvanometer Type R, sens. about $10^{-9}$,amp./mm.

but the substitution of lead covered telephone cable eliminated the leakage. (This cable can be obtained having a guaranteed minimum insulation resistance of 500 megohm miles.)

The tube employed is the Western Electric D–96475 and it is a very definite improvement over the similar tubes previously available. It is mounted, as shown at *T* in Fig. 1, directly in the high vacuum of the mass spectrometer, and is protected by a half-inch of Rema iron from the stray field of the magnet *M*. In this construction the tubulation for the control grid lead is most convenient. The high resistance is mounted on the grid cap along with a small collecting electrode immediately behind the focal slit.

An auxiliary device is employed which gives a continuous indication of magnetic field strength. This takes the form of a plate of diamagnetic material, in this case Acheson graphite, suspended in the upper part of the magnetic field from a torsion balance. The force exerted on the plate tending to push it out of the field is proportional to the square of the field strength, and thus directly proportional to the $m/e$ value of the ion brought to focus by that field strength. A mirror is mounted on the torsion balance for optical reading and the molecular weights so obtained readily fall within one percent of the true values, which is amply close for identification.

An attempt to utilize piano steel wire for the torsion fiber resulted in excessive zero shift due to elastic hysteresis, but the use of pure tungsten wire, even without annealing, has made this effect inappreciable.

The taking of observations involves plotting simultaneously the magnetic balance deflection and the positive ion current to the amplifier against an independent parameter, which for convenience is taken as the resistance inserted in the magnet circuit. This resistance is continuously variable from its maximum value of twenty-two ohms to about one-tenth ohm.

The results are presented in tabular form with one specimen curve from each substance to give a better idea of the form of the results obtained. To facilitate comparisons the peak heights are all given as percentages of the height of the primary peak. The column headed $\mu a$ gives the positive ion current received on the anticathode, the next column shows the electron current received on the grid, and the volts column shows the voltage impressed between the filament and the grid. However, because of interpenetration of the accelerating field for the ion, this is in all cases higher than the true value of the energy possessed by the bombarding electrons. The next column shows the true height in cm of the primary peak, one cm representing a positive ion current to the collector of approximately $10^{-16}$ amp. The pressure in the ionizing chamber was of the order of $10^{-4}$ mm.

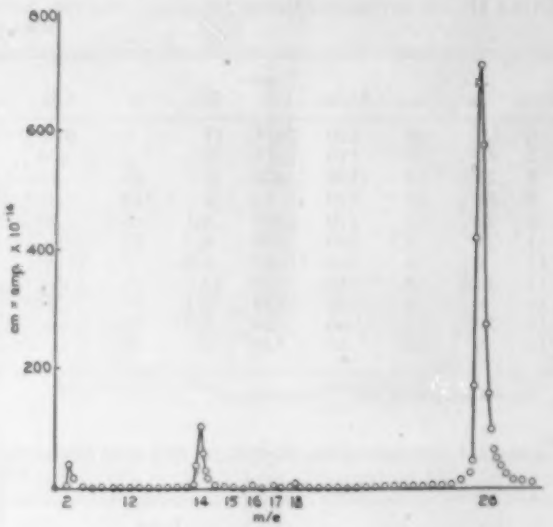


FIG. 4. Run No. 1. Nitrogen. 118 volt electrons. Height of $N_2$ peak = 705 cm.

## NITROGEN

The nitrogen used was prepared by the thermal decomposition of sodium azide $NaN_3$ which is a very convenient source of pure nitrogen. Nitrogen within the voltage range considered yields predominantly molecular ions and shows satisfactory agreement with previous work on this substance. Although the source of the nitrogen precludes any possibility of its contamination with water vapor, nevertheless the walls of the apparatus apparently yield some water vapor and some organic vapor may be present from stopcock grease to account for the hydrogen found. The carbon peak is satisfactorily accounted for in the use of a graphite mounting for the filaments. No satisfactory explanation has been found for the two peaks appearing consistently at 39 and 41. The $NH_3$ and $NH_4$ peaks are certainly enhanced somewhat by OH and $H_2O$ but no separation of the two was possible. The peak corresponding to atomic hydrogen ion was beyond the range of the apparatus so was necessarily omitted. Run No. 1 is shown as Fig. 4. (See Table I.)

TABLE I. *Ion intensities observed for nitrogen bombarded with electrons of various energies. Intensities calculated to basis $N_2^+ = 100$. $\mu a$ = positive ion current incident on anticathode; ma = electron current incident on grid.*

| Run | $\mu a$ | ma | Volts | True $N_2$ | $H_2$ | C | N | NH | $NH_2$ | $NH_3$ | $NH_4$ | CN | $N_2$ | 39 | 41 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 12 | 3 | 118 | 705 | 5.5 | 0.31 | 14 | 0.43 | 0.57 | 0.50 | 1.0 | 0.17 | 100 | 0.17 | 0.26 |
| 2 | 8 | 2 | 100 | 270 | 8.9 | .56 | 18 | .56 | .74 | .67 | 1.1 | .37 | 100 | .37 | .74 |
| 3 | 11 | 3 | 80 | 110 | 8.6 | 2.7 | 29 | .45 | 1.8 | 1.8 | 3.6 | — | 100 | — | 1.8 |
| 4 | 9 | 3 | 60 | 86 | 7.0 | 1.7 | 17 | .46 | 1.2 | 1.2 | 2.1 | — | 100 | — | — |
| 5 | 5 | 7 | 40 | 56 | 13. | — | 2.1 | 1.1 | .9 | 2.0 | 5.4 | — | 100 | — | 1.1 |

TABLE II. *Ion intensities observed for carbon monoxide bombarded with electrons of various energies. Intensities calculated to basis $CO^+ = 100$.*

| Run | μa | ma | Volts | True CO | $H_2$ | C | CH | $CH_2$ | $CH_3$ | O | OH | $H_2O$ | CO | 39 | 41 | $CO_2$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 6 | 9 | 4 | 120 | 2075 | 15 | 1.7 | 0.05 | 0.38 | 0.29 | 0.77 | 0.39 | 1.2 | 100 | 0.10 | 0.14 | 0.63 |
| 7 | 12 | 5 | 120 | 1175 | X | 3.6 | .04 | .43 | .38 | 1.3 | .47 | 1.5 | 100 | .17 | .17 | .60 |
| 8 | 25 | 12 | 120 | 430 | X | 19 | .46 | 1.2 | .58 | 5.8 | .93 | 2.3 | 100 | .35 | .58 | .93 |
| 9 | 50 | 26 | 120 | 14 | X | 370 | 7.0 | 18 | 7.0 | 160 | — | — | 100 | — | — | — |
| 10 | 20 | 12 | 120 | 1560 | 4.5 | 5.1 | .13 | .32 | .22 | 1.2 | .38 | 1.7 | 100 | — | .13 | .06 |
| 11 | 11 | 1.5 | 120 | 130 | 4.2 | 18 | — | — | .6 | 2.3 | 3.8 | 20 | 100 | — | .77 | .54 |
| 12 | 8 | 3 | 100 | 365 | 6.8 | 9.8 | — | .27 | .02 | 3.2 | .6 | 2.1 | 100 | .55 | .44 | .41 |
| 13 | 11.5 | 18 | 80 | 29 | 52 | 21 | — | — | — | 14 | 3.5 | 6.9 | 100 | 2.8 | — | — |
| 14 | 9 | 5 | 80 | 125 | 4.4 | 19 | .8 | .56 | .48 | 6.4 | — | 1.6 | 100 | — | — | — |
| 15 | 10 | 6 | 60 | 60 | 5.3 | 15 | — | — | — | 3.3 | — | 2.5 | 100 | — | — | — |
| 16 | 5 | 10 | 40 | 40 | 3.7 | 5 | — | — | — | 2 | 1.5 | 2.5 | 100 | — | — | — |

X = not covered in run. — = not found.

TABLE III. *Ion intensities observed for ammonia bombarded with electrons of various energies. Intensities calculated to basis $NH_3^+ = 100$.*

| Run | μa | ma | Volts | True $NH_3$ | $H_2$ | C | N | NH | $NH_2$ | $NH_3$ | $NH_4$ | $N_2$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 17 | 10 | 0.1 | 117 | 18 | 14 | 33 | 78 | 8.3 | 86 | 100 | 139 | 680 |
| 18 | 20 | 2.5 | 117 | 7 | 43 | 36 | 190 | 21 | 130 | 100 | 71 | 400 |
| 19 | 9 | 2.5 | 114 | 17.5 | 31 | 7.1 | 7 | 10 | 104 | 100 | 74 | 40 |
| 20 | 19 | 8.5 | 110 | 21 | 76 | 16 | 12 | 12 | 107 | 100 | 100 | 79 |
| 21 | 30 | 11 | 110 | 17 | 47 | 7.3 | 13 | 13 | 130 | 100 | 12 | 35 |
| 22 | 9 | .5 | 97 | 15 | 13 | 33 | 90 | 11 | 93 | 100 | 103 | 640 |
| 23 | 7 | 0.1 | 81 | 9.7 | 7.2 | 26 | 103 | 10.3 | 88 | 100 | 90 | 850 |
| 24 | 9 | 3 | 60 | 5.7 | 70 | 13 | 17 | 20 | 160 | 100 | 26 | 53 |
| 25 | 9 | 2 | 60 | 3.3 | 75 | 45 | 120 | — | 100 | 100 | 100 | 710 |
| 26 | 8.5 | 3.5 | 39 | 3.1 | 19 | — | — | — | 105 | 100 | 32 | 48 |
| 27 | 7.5 | 7.5 | 40 | 1.7 | 60 | 60 | — | — | 60 | 100 | 94 | 590 |

## CARBON MONOXIDE

The carbon monoxide used was prepared by the dehydration with sulphuric acid of formic acid.

An interesting and unexplained effect is shown in runs 7, 8 and 9 which were made consecutively with everything unchanged except the electron current and correspondingly the positive ion current to the anticathode. It seems strange that a fourfold increase in the positive ion current should result in a decrease of the primary peak height to scarcely more than one percent of its initial value. It is presumably this abnormal depression of the CO peak which causes the apparent large increase in the C peak. Run No. 13 was made at a reduced pressure of CO, about one-fourth of the normal pressure of about $10^{-4}$ mm. Run No. 7 is shown as Fig. 5. (See Table II.)

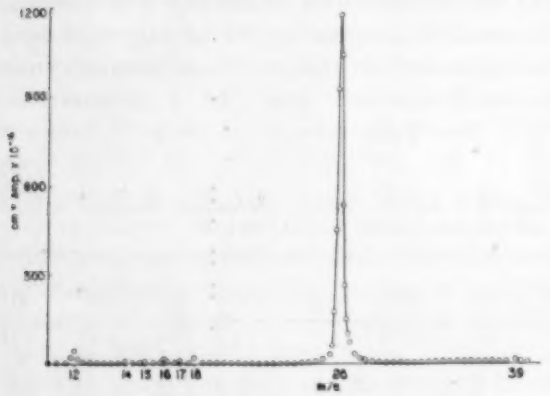


FIG. 5. Run No. 7. Carbon monoxide. 120 volt electrons. Height of CO peak = 1175 cm.

## AMMONIA

The ammonia used was produced by heating a mixture of ammonium sulphate with a large excess of calcium oxide. Runs 21, 24 and 26 were made on a different sample which was further dried with KOH pellets, and show that the first sample was not satisfactorily dried (Fig. 6). It seems likely that the presence of

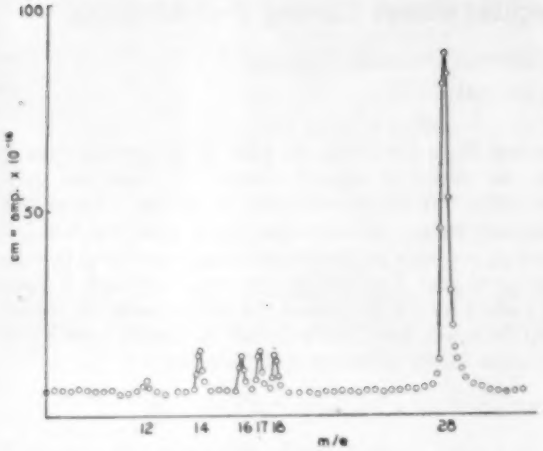


FIG. 6. Run No. 23. Ammonia. 81 volt electrons. Height of $NH_3$ peak = 9.7 cm.

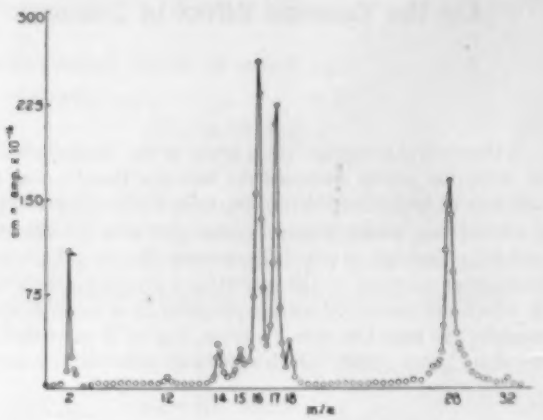


FIG. 7. Run No. 28. Hydrazine. 113 volt electrons. Height of $NH_3$ peak = 222 cm. The peak at 27 is not satisfactorily accounted for.

water vapor contributes to the high intensity observed for the $N_2$ peak, but this point will require further observation. It is to be noted that there is substantial equality between the $NH_2$ and $NH_3$ peaks, as has been reported previously by Bartlett.[2] (See Table III.)

### HYDRAZINE

The sample of hydrazine used was kindly supplied by Professor Beckman of the chemistry department. It had been distilled three times over KOH and then stored for some months in contact with KOH so that its water content must have been far below that contributed by the walls of the apparatus.

Because the tube from which the vapor is released in the filament assembly is necessarily heated by radiation from the filaments, the hydrazine seems to be almost completely thermally decomposed. Thus the primary ion in this case is $NH_3$ and not $N_2H_4$. Run No. 28 is shown as Fig. 7. The entry t in the table means the peak was definitely present but of uncertain height. (See Table IV.)

TABLE IV. *Ion intensities observed for hydrazine bombarded with electrons of various energies. Intensities calculated to basis* $NH_3^+ = 100$.

| Run | μa | ma | Volts | True $NH_3$ | $H_2$ | C | CH | N | NH | $NH_2$ | $NH_3$ | $NH_4$ | CN | 27 | $N_2$ | $N_2H$ | $N_2H_2$ | $N_2H_3$ | $N_2H_4$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 28 | 21 | 7.5 | 113 | 222 | 47 | 2.3 | 0.5 | 14 | 12 | 116 | 100 | 16 | 0.67 | 1 | 72 | t | t | t | 2.7 |
| 29 | 20 | 7 | 114 | 171 | 79 | 1.5 | — | 17 | 14 | 123 | 100 | 6.5 | 1 | 1.5 | 61 | t | t | t | 2.9 |
| 30 | 8 | 4 | 80 | 47 | 49 | — | — | 19 | 13 | 105 | 100 | 7.4 | t | t | 47 | 1.5 | 1 | 2 | 3 |
| 31 | 30 | 15 | 60 | 92 | 27 | 11 | .6 | 6 | 5 | 102 | 100 | 141 | — | — | 84 | t | t | t | 3 |
| 32 | 15 | 10 | 40 | 40 | 57 | 5 | — | 2 | 4 | 81 | 100 | 20 | — | t | 57 | 2 | — | — | — |
| 33 | .9 | 8 | 30 | 4 | 25 | — | — | — | — | 15 | 100 | — | — | — | — | — | — | — | — |
| 34 | 0.1 | 4.7 | 20 | — | — | — | | | | | | | | | | | | | |

Because of their great stability, nitrogen and carbon monoxide yield predominantly molecular ions. However, ammonia and hydrazine decompose readily to yield fractional ions, and can recombine in many different ways depending on collision probability.

Acknowledgment is made to Professor R. A. Millikan, under whose direction this work has been done, for his interest and helpful suggestions.

[2] James H. Bartlett, Jr., Phys. Rev. **33**, 169 (1929).

# On the Zeeman Effect in Diatomic Molecular States Having $L$-Uncoupling

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(Received March 18, 1935)

A theoretical investigation is given of the Zeeman effect in molecular states intermediate between Hund's case $b'$ and case $d'$, which are the limiting cases for small and large $L$-uncoupling, respectively. Zeeman patterns for the $3d$ and $4d$ complexes of the helium molecule are calculated and curves obtained for the variation of overall widths with $K$ which are compared with experiment. For small $K$ the energies are near the case $b'$ curves, but as $K$ increases a breaking away occurs which results in their approaching the case $d'$ curves. When the state in the limiting case $d'$ has the electronic angular momentum quantized antiparallel to the nuclear rotation, a crossing over of the magnetic energy curves takes place with the passage through a state in which the molecule is relatively insensitive to the field. This crossing over occurs between $K$ equal to 4 and 8 for the $\Delta$ states of the helium molecule considered (magnetic field 30,000 gauss). A crossing over which occurs in one of the $\Pi$ states is discussed.

THE experimental work of Millis[1] on the Zeeman effect in ortho-helium bands has shown that a wide variety of patterns is obtainable of a shape intermediate between the shapes of those patterns predicted by Hund's limiting cases for a molecule with electrons having orbital angular momentum. In Hund's case $b'$ the angular momentum vector $L$ is tightly coupled to the axis of figure connecting the nuclei; its component along that axis is quantized and can be designated by the quantum number $\Lambda$. On the other hand in case $d'$ the coupling forces between $L$ and the axis of figure are negligible; $\Lambda$ no longer has meaning as a quantum number. It is now the mechanical angular momentum of the revolving nuclei which is quantized and to which can be assigned the quantum number $R$. In both cases, spin being absent, $K$ represents the quantum number for the total angular momentum of the molecule. The phenomenon of the passage from case $b'$ to case $d'$ as the rotation of the molecule increases is closely related to $\Lambda$-doubling and is called $L$-uncoupling. It has been treated by Hill and Van Vleck, Kronig, Van Vleck, Dieke, Kronig and Fujioka and others.[2] The effect of an external magnetic field has been discussed for the two limiting cases by many authors.[3] In the intermediate case the effective magnetic moment of the molecule varies with $K$, because of the uncoupling, in a way that causes the patterns to depart from both of the limiting shapes. It is the purpose of this paper to present a theoretical investigation of this subject.

## The Perturbation Function

We shall start with case $b'$ as the unperturbed system and neglect all the effects of the spin. In the bands examined by Millis the spin is unresolved and it is quite satisfactory to regard the triplet systems as singlets. This merely means that at quite low fields the Paschen-Back effect becomes total in all the triplet states and therefore the selection rule $\Delta M_s=0$ is rigorously obeyed. The patterns fall on top of each other since the term positions are built up around 0 and $\pm 2\Delta\nu_s$ for all such triplets.

Our perturbation function is the sum of two parts.[4] The first part, $H_1$, is that due to the rotational distortion of the molecule and serves to remove the degeneracy which comes from the fact that $\Lambda$ can be parallel or antiparallel to the axis of figure. The perturbing Hamiltonian consists of certain terms in the Schrödinger equation for the rotating molecule which are usually neglected in separating the electronic and rotational parts of the wave function. We take the value of the matrix elements of this Hamiltonian from Van Vleck[2] or Kronig.[5] It is

[1] Millis, Phys. Rev. **37**, 1005 (1931); **38**, 1146 (1931). See also Crawford, Rev. Mod. Phys. **6**, 112 (1934).

[2] Hill and Van Vleck, Phys. Rev. **32**, 267 (1928); Kronig, Zeits. f. Physik **50**, 347 (1928); Van Vleck, Phys. Rev. **33**, 467 (1929); Dieke, Zeits. f. Physik **57**, 71 (1929); Kronig and Fujioka, Zeits. f. Physik **63**, 168 (1930); Fujioka, Zeits. f. Physik **63**, 175 (1930).

[3] For a general discussion see the article by Crawford, reference 1.

[4] For a similar computation dealing with spin-uncoupling in molecules in a magnetic field, see Hill, Phys. Rev. **34**, 1507 (1929).

[5] Kronig, *Band Spectra and Molecular Structure*, Cambridge, University Press, 1930.

$$H_1(\Lambda, K; \Lambda\pm1, K) = 2(BL_\eta)(\Lambda, \Lambda\pm1)[(K\mp\Lambda)(K\pm\Lambda+1)]^{\frac{1}{2}}, \tag{1}$$

all other elements being zero. In this expression

$$(BL_\eta)(\Lambda, \Lambda\pm1) \equiv \int_0^\infty P_\Lambda^*(r)\left[\frac{L_\eta(\Lambda, \Lambda\pm1)h^2}{8\pi^2cMr^2}\right]P_{\Lambda\pm1}(r)r^2dr, \tag{2}$$

where $P(r)$ is the vibrational wave function of the molecule, $M$ is the reduced mass of the nuclei, $L_\eta(\Lambda, \Lambda\pm1)$ is a matrix element of one of the components of the orbital electronic angular momentum operator $L$ perpendicular to the axis of figure. We can take $L_\eta(\Lambda, \Lambda\pm1)$ as equal approximately to $\frac{1}{2}[L(L+1)-\Lambda(\Lambda\pm1)]^{\frac{1}{2}}$, which multiplied by a kind of a mean value of the rotational constant $B$ gives us the approximate value of the above integral.

For the part due to the external magnetic field, we take the Hamiltonian function

$$H_2 = \Delta\nu_n L_z, \qquad L_z = L_\eta \sin\theta + L_\zeta \cos\theta, \qquad \Delta\nu_n = He/4\pi mc^2. \tag{3}$$

Here $z$ is the direction of the field $H$, $(\xi\eta\zeta)$ is a set of Cartesian axes fixed in the molecule with the origin at the center of gravity of the nuclei. The $\zeta$ axis coincides with the internuclear line, the $\xi$ axis lies in the $xy$ plane, and $\theta$ is the polar angle between the internuclear line and the direction of the field. $L$ is the electronic orbital angular momentum operator of quantum mechanics mentioned above. To obtain the matrix elements of this Hamiltonian, we utilize the integrals given by Reiche and Rademacher[6] for the symmetrical top. We have for the non-zero elements

$$\begin{aligned}
&H_2(\Lambda, K; \Lambda, K) = 2\beta\Lambda^2,\\
&H_2(\Lambda, K; \Lambda+1, K) = -\beta[L(L+1)-\Lambda(\Lambda+1)]^{\frac{1}{2}}[(K-\Lambda)(K+\Lambda+1)]^{\frac{1}{2}},\\
&H_2(\Lambda, K; \Lambda, K+1) = \frac{\Delta\nu_n\Lambda}{K+1}\left[\frac{(K-M+1)(K+M+1)(K-\Lambda)(K+\Lambda+1)}{(2K+1)(2K+3)}\right]^{\frac{1}{2}},\\
&H_2(\Lambda, K; \Lambda+1, K+1)\\
&\quad = [L(L+1)-\Lambda(\Lambda+1)]^{\frac{1}{2}}\frac{\Delta\nu_n}{2(K+1)}\left[\frac{(K-M+1)(K+M+1)(K+\Lambda+1)(K+\Lambda+2)}{(2K+1)(2K+3)}\right]^{\frac{1}{2}},
\end{aligned} \tag{4}$$

where $\beta = \Delta\nu_n M/2K(K+1)$.

The unperturbed energies for case $b'$ are given by the expression

$$W_\Lambda^0 = f(\Lambda) + B[K(K+1)-\Lambda^2+L(L+1)-\Lambda^2], \qquad B = h/8\pi^2cMr_0^2, \tag{5}$$

where $f(\Lambda)$ is the coupling energy of an $L$-complex. If one makes the hypothesis of pure precession, $f(\Lambda)$ becomes $A\Lambda^2$, where $A$ is the coupling constant.

## Calculation of Energies

We shall neglect the terms which are not diagonal in $K$. If the rotational states involved are not close together, in doing this we are neglecting a second order effect in the field which is small. In computing overall widths of Zeeman patterns this second order effect would cancel out because it only gives a shift of the pattern and a distortion of its shape. Classically we are neglecting the effect of that component of the vector $L$ which is perpendicular to the vector $K$. $K$ precesses around the direction of the field and while $L$ precesses rapidly around $K$, still the effect of its perpendicular component does not average out completely for large fields. Actually we cannot expect the rotational energy differences to be always large compared to the Zeeman displacements. However, for extreme magnetic levels ($K$ parallel and antiparallel to the field), the effect of the perpendicular component

[6] Reiche and Rademacher, Zeits. f. Physik **39**, 444 (1926); **41**, 453 (1927).

is a minimum since this component is then approximately perpendicular to the field. The truth of this fact is borne out on examining those elements of our perturbation function which are not diagonal in $K$. They are seen to be smallest for $M=\pm K$. Thus even when the effect of the non-diagonal terms is not small, we see that it can be expected that, excepting under unusual conditions such as two levels very near each other, their effect is not to change greatly the energy differences of levels corresponding to extreme values of $M$, that is the overall widths, but to distort the shape of the energy patterns.

For $L=1$ the secular equation is a cubic which can be solved exactly. The three roots are

$$\begin{aligned} W_{\pm} &= A/2+B(K^2+K+1)+\beta\pm B[\alpha^2/4-\alpha\gamma+\gamma^2(2K+1)^2]^{\frac{1}{2}}, \\ W &= A+B(K^2+K)+2\beta, \end{aligned} \tag{6}$$

where $\alpha=A/B$, $\gamma=1-\beta/B$, $A=f(1)$. If $\alpha>0$, we have a normal $p$-complex and $W_-$ corresponds to the $\Sigma$ state and $W$ and $W_+$ to the two $\Pi$ states. For zero fields these expressions reduce to those given by Hill and Van Vleck for $\Lambda$-doubling. The correlation with case $d'$ is easily found by expanding in inverse powers of $2K+1$ and is given in the papers by Hill and Van Vleck and by Dieke.

In the case of $L=2$, which is of interest in the helium bands, the secular equation is a quintic which can be factored into the following quadratic and cubic determinants

$$\begin{vmatrix} (W_2^0+8\beta-W) & H_p(21) \\ H_p(21) & (W_1^0+2\beta-W) \end{vmatrix}=0, \qquad \begin{vmatrix} (W_2^0+8\beta-W) & H_p(21) & 0 \\ H_p(21) & (W_1^0+2\beta-W) & 2H_p(10) \\ 0 & H_p(10) & (W_0^0-W) \end{vmatrix}=0, \tag{7}$$

where $H_p=H_1+H_2$. The quadratic we can solve at once. For the cubic approximate solutions are obtainable which are good for extreme values of the parameters and which reduce to those given by Dieke[7] for zero field if one makes the hypothesis of pure precession. Since these formulas are rather clumsy, we shall not give them here. However if in these expressions we retain only second order terms in the $L$-uncoupling and first order terms in the field, we obtain the simplified approximate solutions given below in Eqs. (8) and (9). More directly, we can use the simple perturbation theory. Thus for $\alpha$ large, $K$ and $\beta/B$ small, that is near case $b'$, we have ($\alpha>0$, $K\geq 2$)

$$\begin{aligned} W\Delta_a &= 4A+B(K^2+K-2)+4(K^2+K-2)B^2/3A+8\beta[1-4(K^2+K-2)/3\alpha]=W\Delta_b, \\ W\Pi_a &= A+B(K^2+K+4)+8(2K+1)^2B^2/3A+2\beta[1-8(2K+1)^2/3\alpha], \\ W\Pi_b &= A+B(K^2+K+4)-4(K^2+K-2)B^2/3A+2\beta[1+4(K^2+K-2)/3\alpha], \\ W\Sigma_a &= B(K^2+K+6)-12(K^2+K)B^2/A+24\beta(K^2+K)/\alpha. \end{aligned} \tag{8}$$

For near case $d'$, $K$ large, $\alpha$ and $\beta/B$ small, we likewise have

$$\begin{aligned} W\delta_2 &= A+B(K-2)(K-1)+B(12\alpha-3\alpha^2)/4(2K+1)+4\beta(K+1)-\tfrac{3}{4}\beta\alpha^2/(2K+1), \\ W\delta_{-2} &= A+B(K+2)(K+3)+B(12\alpha-3\alpha^2)/4(2K+1)-4\beta K+\tfrac{3}{4}\beta\alpha^2/(2K+1), \\ W\delta_1 &= 5A/2+B(K-1)K+B(36\alpha-9\alpha^2)/8(2K+1)+2\beta(K+3)-(9/8)\beta\alpha^2/(2K+1), \\ W\delta_{-1} &= 5A/2+B(K+1)(K+2)-B(36\alpha-9\alpha^2)/8(2K+1)-2\beta(K-2)+(9/8)\alpha^2/(2K+1), \\ W\delta_0 &= 3A+BK(K+1)-B(12\alpha-3\alpha^2)(2-\alpha)/2(2K+1)^2+6\beta+6\beta\alpha^2(3-\alpha)/(2K+1). \end{aligned} \tag{9}$$

Here we are using the subscript $a$ to indicate the higher energy component of a $\Lambda$-doublet in the normal case and $b$ for the lower energy component. The cubic gives the higher components as well as the $\Sigma$ level to which we have also given the subscript $a$. $\delta$ in Eq. (9) means that it is a $\delta$-complex

[7] See Dieke, reference 2.

($L=2$, case $d'$) and the subscript indicates the quantized value of $L$ along the direction of nuclear rotation. These expressions reduce to the Zeeman expressions for the two cases for limiting values of $\alpha$.

It should be pointed out that we can just as well begin with case $d'$, in which case we assume the interaction Hamiltonian to contain the square of the cosine of the angle between the $L$ vector and the axis of figure. The matrix elements are readily obtained from the relations given in the articles by Van Vleck and Hill. On neglecting the elements not diagonal in $K$, we obtain the same secular equation as by the above method.

In the case of the cubic we have the following simple way of obtaining values for the magnetic energy levels from the zero-field levels. In order to use the data given by Fujioka, we take the unperturbed (case $b'$) energies as approximately

$$W_\Lambda^0 = A_\Lambda + B(K+\tfrac{1}{2})^2 - \beta'(K+\tfrac{1}{2})^4, \qquad \Lambda = 0,\ 1,\ 2. \tag{10}$$

Then if $W_0$, $W_1$, $W_2$ are the zero-field roots of the cubic and if we neglect the squared and cubed terms in $\beta$, we can write our secular equation in the form

$$-(W_0-W)(W_1-W)(W_2-W) = 2\beta[(W_0^0-W)(W_2^0-W)+4(W_0^0-W)(W_1^0-W) - 48B^2K(K+1)\alpha_{10}^2+12BK(K+1)\alpha_{10}(W_2^0-W)+4B(K^2+K-1)\alpha_{12}(W_0^0-W)]. \tag{11}$$

To obtain the energies corresponding to $W_0$, we substitute $W_0$ for $W$ throughout excepting in the first bracket on the left and then solve the resulting linear equation. The $\alpha$'s are constants, nearly unity, introduced and evaluated by Kronig and Fujioka in their zero-field secular determinant so as to get the best fit with experiment. They allow for the fact that $(BP_y)(\Lambda, \Lambda+1)$ in the first part of our perturbation function is not accurately equal to $\frac{1}{2}B[L(L+1)-\Lambda(\Lambda+1)]^{\frac{1}{2}}$.

## Application to the Helium Bands

Experimentally we find that half of the rotational states are missing. This is because $He_2$ is a homonuclear molecule the nuclei of which obey Bose statistics and therefore the allowed states are symmetrical in the nuclei. Since the states we are interested in are also odd ($u$), they are all negative under reflection in the origin and we must omit the positive ones. It is easy to see just which the negative ones are. For $\Sigma_u^+$ states[8] the terms are alternately positive and negative beginning with a positive term for $K=0$. The two rotational terms of a given $K$ for $\Pi$ and $\Delta$ states are always one positive and one negative, any one series in $K$ being alternately positive and negative. Discarding the positive terms, we have remaining three states for $K$ odd and two for $K$ even. These correspond

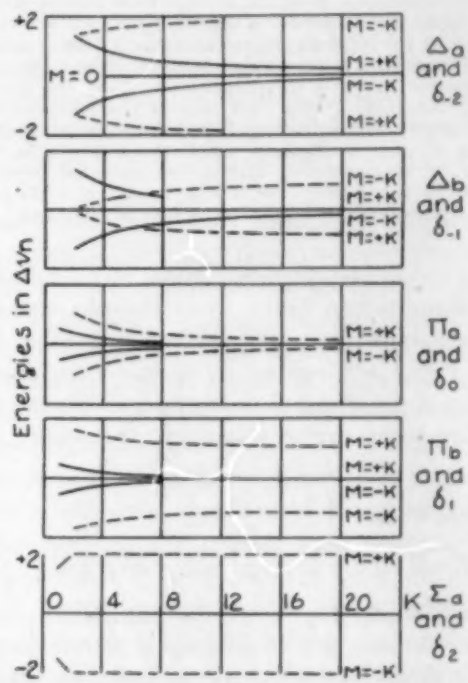


Fig. 1. Magnetic levels of a $d$-complex for the limiting cases drawn around the zero-field energy ($M=0$). Only $M=0$, $\pm K$ levels are plotted. The solid curves are case $b'$ and the broken curves case $d'$. The correlation between the states is that for $\alpha>0$. The energy scale is in units of $\Delta\nu_0$. $K$ is the quantum number associated with the total angular momentum of the molecule.

[8] See Weizel, *Handbuch der Experimental Physik, Bandspektra*, p. 136.

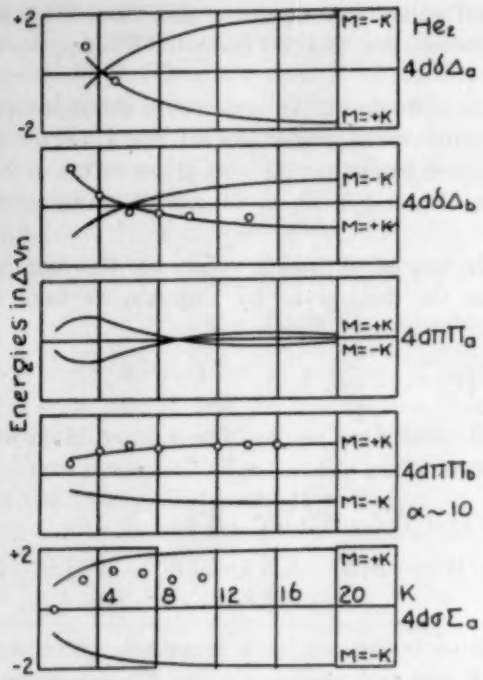


FIG. 2. Magnetic levels of the 4*d* complex of the helium molecule calculated from the present theory using Kronig and Fujioka's constants. $\alpha$ is approximately 10. The crossing over of the levels is due to the passage from quantization of the orbital angular momentum of the electron along the internuclear axis to quantization along the axis of nuclear rotation. During this process the component of the magnetic moment along $K$ passes through zero thus passing through a state in which the molecule is very insensitive magnetically. The circles give the observed widths. In this figure and in Fig. 3, $\Delta\nu_a$ is 2.415 cm$^{-1}$ which corresponds to a field strength of 30,000 gauss.

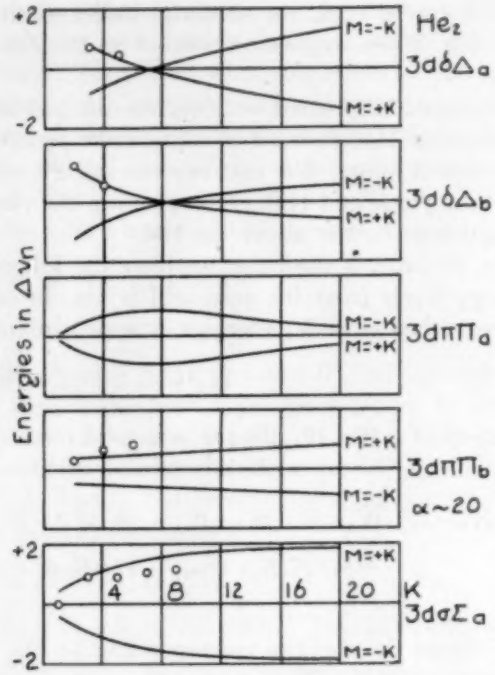


FIG. 3. Magnetic levels of the 3*d* complex of the helium molecule calculated using Kronig and Fujioka's constants. $\alpha$ being about 20, the binding to the internuclear axis is tighter than it is for the states in Fig. 2 and the transition to case *d'* is therefore slower.

to our cubic and quadratic given above because, our Hamiltonian being symmetrical, states of unlike symmetry cannot perturb each other.[9]

In Fig. 1 is given for comparison the overall widths of the magnetic energy levels for the two limiting cases, drawn using the expression

$$E=2\beta\Lambda^2 \tag{12}$$

for case *b'* and

$$E=\beta[K(K+1)+L(L+1)-R(R+1)] \tag{13}$$

for case *d'*. In Fig. 2 are the calculated curves for the 4*d* complex of molecular helium and in Fig. 3 those for the 3*d* complex. All the curves show clearly the rapid change which takes place in passing from case *b'* with low $K$ to case *d'* with high $K$. The change is more rapid for the 4*d* complex since its angular momentum vector is less tightly bound to the axis of figure. The crossing over of the extreme levels occurs when the component of the magnetic moment along $K$ changes its direction with respect to $K$. The circles represent experimental points obtained from Millis' data by interpreting them in the light of the present theory. The values for the overall widths so obtained are not all self-consistent; we have tried to select those values which were the most reliable from the experimental point of view. The differences which exist are perhaps due to intensity distributions and failure to obtain well resolved patterns in some cases.

The $\Pi_a$ states, for which unfortunately there are no experimental data, are of special interest since they are the only states for which the calculated curves do not lie between the limiting curves. An understanding of this behavior is to be found in examining the solutions for small and large $K$ using Eqs. (8) and (9). The equation for

[9] In Mulliken's notation the states $\Delta_a$, $\Delta_b$, $\Pi_a$, $\Pi_b$, $\Sigma_a$ considered in this paper are designated by $\Delta_c$, $\Delta_d$, $\Pi_d$, $\Pi_c$, $\Sigma_c$, respectively. Rev. Mod. Phys. 3, 94 (1931).

$\Pi_a$ shows that for small $K$ the calculated curve for $M=K$ will lie below the limiting case $b'$ curve ($\alpha>0$) and that the difference between the two will increase rapidly with $K$. The equation for $\delta_0$, which is the limiting case for a $\Pi_a$ state with uncoupling, shows that for $\alpha>3$ the calculated curve lies below the limiting curve but that the difference decreases rapidly with increasing $K$. For $M=K$ both limiting curves lie for all $K$ above the curve for $M=0$. The calculated curves start out for small $K$ below the first limiting curve and then approach the second limiting curve from below. For the $4d\pi\Pi_a$ state the extreme levels cross over at about $K=10$. For $\alpha$ slightly greater than 20, the extreme levels would cross over first for small $K$ and a second time for very large $K$.

Curves of a similar nature could be drawn for the magnetic levels of the three states of a $p$-complex using Eq. (6). The $\Pi$ state correlated to the $\delta_{-1}$ state would show a crossing over of the levels for suitable $\alpha$ and $K$ in a manner very similar to that shown in the cases described above.

The writer wishes to express his sincere thanks to Professor Kemble and Professor Van Vleck for valuable suggestions and criticisms on this work.

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# On Perturbed Series, Especially in C III, B I and O IV

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Consideration of possible extra-configurational perturbations in atomic spectral series shows that often some series are preferable to others for the determination of series limits. In particular: In C III, several $2snd\ ^3D$ terms are recalculated, but Edlén's series limit value is verified in spite of perturbations; in B I, the term values are increased by 90 cm$^{-1}$ or 0.011 volt, so that B I $2s^2 2p\ ^2P_{\frac{1}{2}}$ – B II $2s^2\ ^1S_0$ = 66,930 cm$^{-1}$ = 8.257 volts; and in O IV, the old $5s\ ^3S_1$ term is replaced by a new one at 85,440 cm$^{-1}$, $?4p\ ^3P$ and $?6f\ ^3F$ are repudiated, and $?7f\ ^3F$ and $?8f\ ^3F$ are verified.

ALTHOUGH the term values in most of the spectra of the lightest elements have recently been determined with a high degree of accuracy and completeness by Edlén,[1] there are a few instances in which series limits may be slightly altered and term assignments reconsidered after a study of the influence of extra-configurational perturbing terms.[2, 3] The purpose of this note is to point out the general preferability of some series over others in the determination of series limits, and to make minor alterations in three of Edlén's spectra.

An irregular relationship between the term values and the corresponding quantum defects for a spectral series generally is an indication of the presence of a perturbing series, of which usually only one or two terms appreciably affect the series in question. The extra-configurational series members have the same Laporte parity and (in the $LS$ coupling case, which is all that need be considered in Edlén's spectra) the same multiplicity and $L$ value as the series under consideration. Irregularity arises when the two series overlap or nearly overlap, in which case the members of the one series share their properties with neighboring members of the other with a consequent ambiguity as to configuration. Thus the members of a series may show an energy trend leading toward a false series limit, even though the term or terms mainly responsible for the complication may remain undiscovered. Although perturbing terms can be pointed out for almost all of Edlén's spectral series, we shall list here only those cases in which an analysis appears to lead to definite improvements in term values.

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[1] B. Edlén, Nova Acta Reg. Soc. Scient. Upsaliensis, Ser. IV **IX**, No. 6 (1933).
[2] A. G. Shenstone and H. N. Russell, Phys. Rev. **39**, 415 (1932).
[3] N. G. Whitelaw, Phys. Rev. **44**, 544 (1933).

C III: The $2snd\ ^3D$ series has been used to determine the series limit for C III. In the case of series members for $n \geqq 7$, it seems impossible to assign $J$ values and consequently the energies should be calculated with respect to the center of gravity of the $2s2p\ ^3P$ term. If this is done one obtains the following recalculated term values:

| | $\nu$ | $n^*$ |
|---|---|---|
| $2s7d\ ^3D$ | 20,575 cm$^{-1}$ | 6.9283 |
| $8d$ | 15,722 | 7.9258 |
| $9d$ | 12,412 | 8.9202 |

The resulting $n-n^*$ *versus* $\nu$ plot exhibits quite a curvature near $\nu=0$ as is to be expected because of the presence of the $2p4p\ ^3D$ term near the series limit. The reason for the smallness of the shift of the $2s3d\ ^3D$ term due to perturbation by $2p3p\ ^3D$ is not apparent. In spite of the perturbations present, the $^3D$ series is probably the most reliable from which to determine the series limit because of its length. The $^1F$ and $^3F$ series are very badly perturbed as is easily seen from the variation of the quantum defect with $\nu$. Also the separation of the components of $2s4f\ ^3F$ would be nearly zero except that because of the perturbation, the term acquires part of the multiplet width of $2p3d\ ^3F$.

B I: The series limit of B I was determined by Selwyn.[4] He fitted both the $^2S$ and $^2D$ series to a Ritz formula and took an average value for the series limit. However, upon examination of the series, one finds that a term, $2s2p^2\ ^2S$ lies near to the $5s\ ^2S$ series member and undoubtedly perturbs that term. The $2s2p^2\ ^2S$ term has not been found experimentally but by examining the $2s-2p$ energy differences in members of the isoelectronic sequence, one can place it within the range 5000 to 9000 cm$^{-1}$, whereas $5s\ ^2S$ lies in the neighborhood of 6694 cm$^{-1}$. The $nd\ ^2D$ series is perturbed by a $2s2p^2\ ^2D$ term which lies much deeper than any of the $^2D$ regular series members and consequently the $^3D$ series is not seriously perturbed. It seems more reasonable therefore to determine a series limit from the $^2D$ series alone, and if this is done, we find a value about 90 cm$^{-1}$ greater than the Selwyn value.

O IV: The series limit of O IV is quite accurately determined by the (experimentally) unperturbed $^2D$ series. However, several other series are badly perturbed, and we think involve several wrong classifications. (a) The quantum defect of the $5s\ ^2S$ term as classified is impossible. The perturbing term, $2s2p3p\ ^2S$ lies below $4s\ ^2S$ and consequently should not affect $5s\ ^2S$ as much as $4s\ ^2S$. We have identified a line[5] of intensity $=1$, $\lambda=185.544$A, $\nu=538{,}956$ cm$^{-1}$, attributed by Edlén to O IV on experimental grounds, which we think gives a more probable quantum defect for the $5s\ ^2S$ term. The new term value for $5s\ ^2S$ becomes 85,440 cm$^{-1}$. (b) Edlén questions his classification of $4p\ ^2P$ and one can reason that it must be wrong since the relative quantum defect for $3p\ ^2P$ and $4p\ ^2P$ is opposite to what it should be, because of the presence of the perturbing $2s2p3s\ ^2P$ term between them. (c) Edlén also questions his $nf\ ^2F$ terms for $n \geqq 6$. The terms for $n=7$ and $n=8$ seem all right but $6f\ ^2F$ must be wrong. The nearest perturbing term, $2s2p4d\ ^2F$, lies just below $8f\ ^2F$, and $2s2p3d\ ^2F$ lies below $4f\ ^2F$ so the abnormal quantum defect of the present $6f\ ^2F$ term would seem to disqualify it.

It is easy to determine what series are likely to be free from disturbance by extra members in any particular case, although there seems to be no rule for them except to study the list of terms yielded by each configuration.

[4] E. H. W. Selwyn, Proc. Phys. Soc. **41**, 392 (1929).

[5] B. Edlén, Zeits. f. Physik **85**, 85 (1933).

# The Normal Helium Atom

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A least-squares criterion for the goodness of approximate wave functions is proposed. The root-mean-square energy deviation for the six-term Hylleraas function is calculated to be 3.5 volts. It is shown that no ascending power series in the variables $r_1$, $r_2$ and $r_{12}$ can be a formal solution of the Schrödinger equation.

THE problem of determining the Schrödinger eigenfunction and eigenvalue for the lowest state of helium is one of fundamental importance to the theory of atomic structure; if it were solved, we should know whether or not the present formulation of the nonrelativistic many-body problem is correct. The subject has received the attention of several writers, notably Slater,[1] Kellner[2] and Hylleraas.[3, 4, 5] Slater, by numerical methods, arrived at an eigenvalue for the atom and a charge density for an $s$-electron, but did not represent the wave function analytically; Kellner and Hylleraas used the Ritz variational procedure, in which one guesses at the form of the eigenfunction $\psi$ and allows certain parameters to vary so as to minimize the integral $\int\psi H\psi d\tau$. The latest work on this by Hylleraas[5] resulted in an approximate eigenvalue lower than the experimental term value by an amount which could be attributed to relativistic effects.

The Ritz method results in an upper bound to the true eigenvalue; a lower bound has been sought by Weinstein[6, 7] and MacDonald.[8] Since their methods seem somewhat difficult to justify rigorously, we shall in the present paper try to show how a least-squares method can aid one in judging the relative merits of different approximate wave functions. In addition, we propose to prove that no eigenfunction of the Hylleraas type can be even a *formal* solution of the wave equation.

The method of least squares suggested by Boussinesq[9] consists in adjusting the constants in an approximating function $\psi$ so as to make the integral $I=\int[H-E)\psi]^2d\tau$ as small as possible.[10] Let us set $(H-E)\psi=\epsilon\psi$, where $\epsilon$ will in general be a function of $x$, $y$ and $z$. For any approximate eigenvalue $E$, $\epsilon(x, y, z)$ is an indication of how well the wave equation is satisfied at any point. The integral $I=\int\psi^2\epsilon^2d\tau$ may then be looked upon as a mean square energy deviation.[11] We shall calculate its value, using an eigenfunction due to Hylleraas.

For convenience in computation, the final eigenfunction given by Hylleraas in reference 4 will be used. A further refinement was made in reference 5, but the value of $E$ was lowered by only 0.013 volt, so presumably the value of $I$ would not be influenced much by such a change.

The wave function is, then, $\psi=\varphi(ks, kt, ku)$, where

$$\varphi(s, t, u)=e^{-s/2}[c_0+c_1u+c_2u^2+c_3s+c_4s^2+c_5t^2].$$

The variables are $s=r_1+r_2$, $t=-r_1+r_2$ and $u=r_{12}$; the constants are $c_0=1$, $c_1=0.0972$, $c_2=0.0097$, $c_3=-0.0277$, $c_4=0.0025$, $c_5=-0.0024$, and $k=(L/2M)=0.9089645$.

Since it is purely a routine matter to apply $H$ to this wave function and to calculate $\int(H\psi)^2d\tau$, we shall give only the result. The value of this integral is 2.1115. If $I$ be minimized[12] with respect to $E$, then $E=\int\psi H\psi d\tau$, and $I=\int(H\psi)^2d\tau-E^2$. The constants in $\psi$ may now be varied to

[1] J. C. Slater, Phys. Rev. **32**, 349 (1928).
[2] G. W. Kellner, Zeits. f. Physik **44**, 91 (1927).
[3] E. A. Hylleraas, Zeits. f. Physik **48**, 469 (1928).
[4] E. A. Hylleraas, Zeits. f. Physik **54**, 347 (1929).
[5] E. A. Hylleraas, Zeits. f. Physik **65**, 209 (1930).
[6] D. H. Weinstein, Phys. Rev. **40**, 737 (1932); Phys. Rev. **41**, 839 (1932).
[7] D. H. Weinstein, Proc. Nat. Acad. Sci. **20**, 529 (1934).
[8] J. K. L. MacDonald, Phys. Rev. **43**, 830 (1933); Phys. Rev. **46**, 828 (1934).
[9] J. Boussinesq, *Theorie de la chaleur* (I), p. 316.
[10] We should like to express our appreciation to Mr. R. K. Cook for calling our attention to this method.
[11] One could, alternatively, weight the square of the deviation $\epsilon\psi$ to emphasize regions where the eigenfunction is large.
[12] This fixes the relation between $E$ and the constants $c_0\cdots c_5$. Up to this point $E$ can be assumed as independent of the constants.

make either $E$ or $I$ a minimum. (One would in general expect that $E$ and $I$ do not take on minimum values simultaneously, since the wave function used is only an approximate one.) We shall suppose it is $E$ that is made a minimum. The value given by Hylleraas is $E=-1.45162\ Rh$, so that $I=0.0043$. It follows that $I^{\frac{1}{2}}=0.065\ Rh$, corresponding to about 3.5 electron volts. This root-mean-square deviation would vanish if the wave function were actually a solution of the differential equation.

One cannot, however, necessarily assert that the true eigenvalue lies about 3.5 electron volts below that calculated by Hylleraas. The r.m.s. deviation may be viewed simply as a measure of the goodness of the approximate wave function used. That is, if two different approximate functions should give the same value of $E$, then one would suppose that function with the smallest r.m.s. deviation to be the better of the two.

Since the actual deviation for some regions of space will in general be larger than the r.m.s. deviation, it seems to us that the above value of 3.5 electron volts is not small. It can be easily verified, in fact, that the deviation becomes *infinite* at any of the singularities, $r_1=0$, $r_2=0$, or $r_{12}=0$. The eigenfunction is thus probably very badly in error in the general neighborhood of any of these points. This prompts an investigation of the relationship of the function to the differential equation. It might seem that matters would be improved by using a power series instead of a polynomial (times an exponential factor). We shall now prove that no series in ascending powers of $r_1$, $r_2$ and $r_{12}$ can be a formal solution of the wave equation.

For convenience, put $x=r_1$, $y=r_2$ and $z=r_{12}$. the wave equation is then:

$$\psi_{xx}+(2/x)\psi_x+\psi_{yy}+(2/y)\psi_y+2\psi_{xz}+(4/z)\psi_z$$
$$+[(x^2-y^2+z^2)/xz]\psi_{xz}+[(y^2-x^2+z^2)/yz]\psi_{yz}$$
$$+[(\lambda/4)+(1/x)+(1/y)-(1/2z)]\psi=0.$$

If we expand, $\psi=\sum_0^\infty c_{lmn}x^l y^m z^n$, substitute, and equate coefficients of powers, we find the recursion formula,

$$(l+2)(l+3+n)c_{l+2,\,m,\,n}$$
$$+(m+2)(m+3+n)c_{l,\,m+2,\,n}$$
$$+(n+2)(2n+6+l+m)c_{l,\,m,\,n+2}$$
$$-(l+2)(n+2)c_{l+2,\,m-2,\,n+2}$$
$$-(m+2)(n+2)c_{l-2,\,m+2,\,n+2}+(\lambda/4)c_{lmn}$$
$$+c_{l+1,\,m,\,n}+c_{l,\,m+1,\,n}-\tfrac{1}{2}c_{l,\,m,\,n+1}=0.$$

Substitution of various sets of values of $l$, $m$, and $n$ will result in specific relationships enabling us to determine the $c_{lmn}$'s. We list a few as follows:

$$l=-1,\ m=2,\ n=-1\ ;\ c_{101}=0,$$
$$l=-1,\ m=0,\ n=0\ ;\ 2c_{100}+c_{000}=0,$$
$$l=1,\ m=0,\ n=-1\ ;\ 5c_{101}-\tfrac{1}{2}c_{100}=0.$$

Assuming that $c_{000}=1$, we thus obtain on the one hand $c_{101}=0$ and on the other $c_{101}=-(1/20)$. The fact that at least two inconsistent values of the same coefficient may be obtained means that the power series in question will not satisfy the differential equation, even formally.

In our opinion, the fact that a minimum value of $E$ exists for functions of the Hylleraas type does not shut out the possibility that appreciably lower values of $E$ may result from a use of functions which come closer to satisfying the differential equation. To improve the existing situation one may either construct functions with lower values of $E$ and $I$, or else look for exact solutions. Attempts along the latter line are now being made. It turns out to be rather easy to find formal solutions, and whatever difficulties there are come in with the imposition of the boundary conditions.

# Atomic Wave Functions for Some Excited States of Helium

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Normalized one-electron wave functions and the corresponding fields and energy parameters have been computed by the self-consistent field method for the following excited states of helium: $(1s)^2$, $(1s)(2s)$, $(1s)(2p)$, $(2s)^2$, $(2p)^2$ and $(2s)(2p)$. The results have been compared with those obtained by other methods and with experimental values.

## INTRODUCTION

THE "self-consistent field" method of calculating atomic wave functions has been applied successfully to a number of atoms. So far as the authors are aware the following constitutes a reasonably complete list. $O^{+3}$ to O, Ne, $Na^+$, $Si^{+4}$, $Cl^-$, $K^+$, $Cu^+$, $Cs^+$ have all been computed by D. R. Hartree and collaborators[1] with high accuracy. He, Li and $Li^+$, $Be^+$, $Be^{+3}$ and Be, B, $B^{+2}$ and $B^{+3}$, $F^-$ and F, $Ca^{+2}$, C, N, Na and Hg have been calculated with less emphasis on extreme accuracy.[2] Rather recently $Si^{+2}$ and $Si^{+3}$ have been worked out approximately by H. L. Donley at Brown University (at present unpublished).

The present paper contains the results of similar calculations for certain excited states in helium. Wave functions for some excited states in helium-like atoms have already been obtained[3] by the use of variational methods. Opportunity is taken here to compare the results of the "self-consistent field" calculations both as to wave functions and energy parameters with those of other methods.

## METHOD OF THE CALCULATIONS

The method of the "self-consistent field" has been described so often[4] and is now so familiar, that it is unnecessary to redescribe it in detail here. The limitations of the method have also been amply dealt with elsewhere.[5] We shall content ourselves with discussing briefly the technique used in the application of the method in the present calculations.

The states of helium investigated are: $(1s)^2$ (already worked out by Hartree, but repeated for the sake of completeness and to tabulate the wave function using smaller intervals of $(r)$, $(1s)(2s)$, $(1s)(2p)$, $(2s)^2$, $(2p)^2$ and $(2s)(2p)$.

The only important point in which the method used in this paper differs from that recommended by Hartree is that direct integration was used throughout in preference to the so-called variation method* in obtaining the join of the inward and outward integrations of the appropriate Schrödinger equation. The extra work involved in this procedure was probably compensated for by the greater assurance of the elimination of errors. In any case the labor involved is by no means so great as might at first be thought. The successive approximations to the self-consistent field were in general made in each case by using the final field of the previous approximation. An important consideration is, of course, the assumption of the initial field, i.e., the initial $Z_p$ (the effective nuclear charge for potential.† Several schemes have been investigated. The one generally followed may be briefly summarized as follows.

The wave function of $He^+$ in the $(1s)$ state was first tabulated and the corresponding field calculated. This at once provided an approximate initial $Z_p$ for the $(2s)$ electron in the singly excited $(1s)(2s)$ state. From the distribution of

[1] See, for example, Hartree, Proc. Roy. Soc. **A141**, 282 (1933) for a good survey of the method and some results. Hartree and Black, Proc. Roy. Soc. **A139**, 311 (1933); Hartree, Proc. Roy. Soc. **A143**, 506 (1934); J. McDougall, Proc. Roy. Soc. **A136**, 549 (1932); **A138**, 550 (1932).

[2] Hartree, Proc. Camb. Phil. Soc. **24**, 89 (1928); J. Hargreaves, Proc. Camb. Phil. Soc. **25**, 75 (1929); F. W. Brown, J. H. Bartlett and C. G. Dunn, Phys. Rev. **44**, 296 (1933); Hartree, Phys. Rev. **46**, 738 (1934); C. C. Torrance, Phys. Rev. **46**, 388 (1934); E. H. Kennard and E. Ramberg, Phys. Rev. **46**, 1034 (1934).

[3] See, for instance, C. Eckart, Phys. Rev. **36**, 878 (1930); J. P. Vinti, Phys. Rev. **37**, 448 (1931); F. G. Fender and J. P. Vinti, Phys. Rev. **46**, 77 (1934). Also E. A. Hylleraas, see reference 12.

[4] e.g., Hartree, Proc. Camb. Phil. Soc. **24**, 89 (1928).

[5] J. C. Slater, Phys. Rev. **35**, 210 (1929); V. Fock, Zeits. f. Physik **61**, 126 (1930).

* Cf. Hartree, reference 4, p. 95.

† Cf. Hartree, reference 4, p. 115.

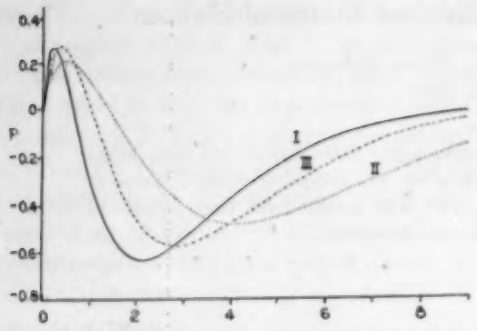


FIG. 1. Plot of the normalized wave function $P$.

charge of the $(2s)$ electron the initial $Z_p$ for the $2s$ electron in the state $(2s)^2$ was computed. Similarly the distribution of charge for the $(1s)$ electron in the $(1s)(2s)$ state was used to compute an initial $Z_p$ for the $(2p)$ electron in $(1s)(2p)$, and the $(2s)(2p)$ case was handled by starting from $(2s)^2$ and the $(2p)^2$ case from $(2s)(2p)$. The number of successive approximations required to attain self-consistency in these various cases varied from two to nine.

An alternative method of estimating the initial $Z_p$ holding out some promise of value consisted in extrapolating the wave functions for the atoms in the second period of the natural system as calculated by Brown, Bartlett and Dunn.[5] If the reciprocals of the positions of the maxima for the $(2s)$ wave functions from boron to neon as given by them are plotted and extrapolated to beryllium, a "stretch" factor may be obtained allowing one to compute very simply the normalized $(2s)$ wave function for beryllium, which has in the normal state 2 $(1s)$ electrons and 2 $(2s)$ electrons. The latter move in the field of a nucleus of 4 positive charges and the 2 $(1s)$ electrons. Hence to a first approximation the field for large $r$ at least may be considered to be like that for the $(2s)$ electrons in helium. This choice proves to be a rather satisfactory one as Fig. 1 shows. This presents the plot of the normalized wave function $P$ corresponding to the assumption just indicated (curve $I$) compared with that obtained by using the initial $Z_p$ from the method described in the previous paragraph (curve $II$) and with the final $P$ function (curve $III$) for the $(2s)^2$ state. In this case the alternative method yields a rather better first approximation.[6]

## RESULTS AND DISCUSSION

The principal results of the calculations are exhibited in Tables I, II, III and IV, presenting,

[6] In this connection it may be remarked that a study was made of the use of the Fermi statistics as applied by Baker (cf. E. Fermi, Zeits. f. Physik **48**, 73 (1928); E. B. Baker, Phys. Rev. **36**, 630 (1930)) to ions of any order. This showed that for the heavier atoms the values obtained from Baker's table provide an excellent initial field for Hartree calculations. In particular in the case of $Si^{+4}$ the former values of $Z_p$ agree with those for the self-consistent field to within a maximum deviation of 2 percent.

TABLE I. *Normalized wave functions ($P$) for helium.*

| $r$ | $(1s)^2$ | $(1s)(2s)$ | | $(2s)^2$ | $(2s)(2p)$ | | $(2p)^2$ | $(1s)(2p)$ | |
|---|---|---|---|---|---|---|---|---|---|
| | $(1s)$ | $(1s)$ | $(2s)$ | $(2s)$ | $(2s)$ | $(2p)$ | $(2p)$ | $(1s)$ | $(2p)$ |
| 0.00 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| .05 | .2152 | .2540 | .0549 | .0767 | .0701 | .0023 | .0021 | .2556 | .0007 |
| .10 | .3900 | .4597 | .0993 | .1382 | .1265 | .0089 | .0079 | .4626 | .0025 |
| .15 | .5308 | .6240 | .1349 | .1864 | .1705 | .0190 | .0160 | .6279 | .0055 |
| .20 | .6428 | .7530 | .1628 | .2228 | .2038 | .0322 | .0286 | .7576 | .0093 |
| .3 | .7984 | .9234 | .1999 | .2654 | .2429 | .0656 | .0582 | .9304 | .0193 |
| .4 | .8853 | 1.0110 | .2178 | .2759 | .2526 | .1057 | .0938 | 1.0157 | .0317 |
| .5 | .9241 | 1.0358 | .2213 | .2620 | .2403 | .1497 | .1329 | 1.0396 | .0459 |
| .6 | .9296 | 1.0189 | .2141 | .2303 | .2118 | .1954 | .1736 | 1.0215 | .0617 |
| .7 | .9123 | .9746 | .1989 | .1859 | .1719 | .2413 | .2145 | .9759 | .0785 |
| .8 | .8798 | .9134 | .1778 | .1330 | .1242 | .2859 | .2545 | .9134 | .0962 |
| .9 | .8374 | .8427 | .1522 | .0750 | .0720 | .3284 | .2927 | .8416 | .1145 |
| 1.0 | .7893 | .7650 | .1233 | .0144 | .0174 | .3681 | .3287 | .7650 | .1332 |
| 1.2 | .6859 | .6202 | .0601 | −.1065 | −.0919 | .4371 | .3924 | .6166 | .1709 |
| 1.4 | .5836 | .4869 | −.0069 | −.2184 | −.1940 | .4913 | .4440 | .4826 | .2081 |
| 1.6 | .4891 | .3746 | −.0737 | −.3155 | −.2838 | .5306 | .4836 | .3700 | .2440 |
| 1.8 | .4054 | .2837 | −.1377 | −.3953 | −.3592 | .5561 | .5117 | .2794 | .2776 |
| 2.0 | .3331 | .2122 | −.1972 | −.4576 | −.4198 | .5696 | .5298 | .2084 | .3085 |
| 2.2 | .2718 | .1572 | −.2514 | −.5034 | −.4664 | .5728 | .5390 | .1539 | .3364 |
| 2.4 | .2205 | .1155 | −.2995 | −.5345 | −.5002 | .5676 | .5408 | .1128 | .3609 |
| 2.6 | .1780 | .0843 | −.3413 | −.5528 | −.5227 | .5557 | .5365 | .0822 | .3821 |
| 2.8 | .1431 | .0612 | −.3768 | −.5603 | −.5355 | .5388 | .5272 | .0595 | .4000 |
| 3.0 | .1147 | .0442 | −.4061 | −.5590 | −.5400 | .5180 | .5140 | .0429 | .4145 |
| 3.2 | .0916 | .0318 | −.4296 | −.5507 | −.5378 | .4946 | .4978 | .0308 | .4258 |

| $r$ | $(1s)^2$ | $(1s)(2s)$ | | $(2s)^2$ | $(2s)(2p)$ | | $(2p)^2$ | $(1s)(2p)$ | |
|---|---|---|---|---|---|---|---|---|---|
| | $(1s)$ | $(1s)$ | $(2s)$ | $(2s)$ | $(2s)$ | $(2p)$ | $(2p)$ | $(1s)$ | $(2p)$ |
| 3.4 | .0729 | .0228 | −.4474 | −.5368 | −.5300 | .4695 | .4795 | .0220 | .4341 |
| 3.6 | .0580 | .0163 | −.4606 | −.5187 | −.5178 | .4434 | .4591 | .0157 | .4396 |
| 3.8 | .0460 | .0116 | −.4690 | −.4976 | −.5021 | .4168 | .4379 | .0112 | .4425 |
| 4.0 | .0364 | .0082 | −.4733 | −.4742 | −.4837 | .3904 | .4160 | .0079 | .4430 |
| 4.4 | .0227 | .0042 | −.4713 | −.4241 | −.4419 | .3390 | .3717 | .0040 | .4376 |
| 4.8 | .0140 | .0021 | −.4582 | −.3729 | −.3967 | .2913 | .3283 | .0020 | .4254 |
| 5.2 | .0086 | .0010 | −.4369 | −.3235 | −.3511 | .2480 | .2873 | .0010 | .4078 |
| 5.6 | .0053 | .0005 | −.4102 | −.2776 | −.3073 | .2096 | .2495 | .0005 | .3864 |
| 6.0 | .0032 | $.0002_5$ | −.3801 | −.2361 | −.2663 | .1761 | .2152 | $.0002_5$ | .3625 |
| 6.8 | .0012 | .0001 | −.3162 | −.1669 | −.1953 | .1223 | .1573 | .0001 | .3110 |
| 7.6 | .0004 | .0000 | −.2546 | −.1153 | −.1398 | .0835 | .1128 | .0000 | .2596 |
| 8.4 | .0001 | | −.1990 | −.0782 | −.0981 | .0562 | .0797 | | .2119 |
| 9.2 | .0000 | | −.1537 | −.0523 | −.0677 | .0374 | .0556 | | .1699 |
| 10.0 | | | −.1163 | −.0345 | −.0462 | .0246 | .0384 | | .1342 |
| 12 | | | −.0548 | −.0117 | −.0170 | .0084 | .0146 | | .0706 |
| 14 | | | −.0243 | −.0038 | −.0059 | .0028 | .0054 | | .0351 |
| 16 | | | −.0104 | −.0012 | −.0020 | .0009 | .0019 | | .0168 |
| 18 | | | −.0043 | −.0004 | −.0007 | .0003 | .0007 | | .0078 |
| 20 | | | −.0017 | −.0001 | −.0002 | .0001 | .0002 | | .0035 |
| 22 | | | .0007 | .0000 | $-.0000_6$ | .0000 | .0001 | | .0016 |
| 24 | | | .0003 | | −.0000 | | .0000 | | .0007 |
| 26 | | | .0001 | | | | | | .0003 |
| 28 | | | .0000 | | | | | | .0001 |
| 30 | | | | | | | | | .0001 |

TABLE Ia. *Values of $P/r^{l+1}$ for small r.*

| r | $(2s)(2p)$ $(^2p)$ | $(2p)^2$ $(^2p)$ | $(1s)(2p)$ $(^2p)$ |
|---|---|---|---|
| 0.00 | 0.00000 | 0.00000 | 0.00000 |
| .05 | .04583 | .04143 | .01336 |
| .10 | .08721 | .07884 | .02547 |

respectively, the normalized wave functions ($P$ values) for the various excited states, the contributions to $Z$ (the effective nuclear charge for field intensity) of the various electrons, their contributions to $Z_p$,[7] and finally the values of the one-electron parameter $\epsilon$. The figures in the first three tables are given to four decimal places, the accuracy of the computations being such that any error in $P$ may be expected not to exceed 2 in the fourth place, and any error in $Z$ or $Z_p$, 1 in the fourth place.[8] All values in the tables have actually been found by straightforward calculation: none has been interpolated. In fact the intervals used in the computation were in general half the size of those given in the tables. Table I(a) contains the values of $P/r^{l+1}$ for small $r$ in the case of the $2p$ electrons: these are of value in starting the outward integration. Corresponding values for the $(1s)$ and $(2s)$ states need not be tabulated since they can be computed with sufficient accuracy directly from $P$.

It may be noted in passing that the values of $Z$ and $Z_p$ for $(1s)^2$ do not agree precisely with those of Hartree (first paper in reference 2; note that the values there quoted refer to the two electrons and must be divided by 2 for comparison with those of the present paper). It should be remarked that Hartree in the case of helium limited the consistency between initial and final fields to 2 in the third decimal place which falls considerably short of the standard of accuracy set in the present paper. Incidentally as a check on the accuracy throughout the work, $\int_0^\infty dr \int_r^\infty P^2/r\,dr$ has been calculated for each electron. This gives $Z_p$ for $r=0$ which should be unity for each electron. In the present work, it does so in every case to within 5 in the *fifth* decimal place.

[7] Strictly speaking these are unnecessary. Their utility, however, dictates their inclusion here. Cf. Hartree, reference 1.

[8] This means of course that the maximum error to be expected in the *total* $Z$ and $Z_p$ (not tabulated since they are readily obtainable by summing the contributions of the individual electrons) is 2 in the fourth decimal place.

The values of $\epsilon$ in Table IV are given in general to three decimals and may be assumed to be correct to that place: the extra place used in obtaining them has been discarded. Those values listed to four decimal places are expected to be in error by no more than 2 in the last place and the error for the $(1s)(2s)$ and $(1s)(2p)$ is probably considerably less. Table IV also includes $-2v_0^*$ and values of $\epsilon$ computed by other methods as mentioned in the Introduction. Comparison with experimental results is rather difficult since the latter are usually given in terms of the ionization energy of the atom in a given state[8a] while the present values are one-electron energy parameters. These can of course be used in connection with the wave functions to compute the total atomic energy values (cf. Hartree and Black[2]). For $(1s)^2$, $(2s)^2$ and $(2p)^2$ this calculation can be carried out approximately by assuming that $\epsilon$ itself is a good approximation to the ionization energy. The computed total energy for these three states then appears as 5.836, 1.4606 and 1.3861, respectively. The experimental value is known definitely only for the first and is 5.808. Some evidence with respect to the second is at hand in the recent experiments of Whiddington and Priestley[9] on energy losses in inelastic collisions in helium. Their work indicates a loss of $59.25 \pm 0.12$ volts in a single collision of an electron with a helium atom. Now the difference between the total energy in the $(1s)^2$ state (5.808) and that in the $(2s)^2$ state (1.4606) is 4.347, corresponding to 58.81 volts, which is very close to Whiddington and Priestley's value, making it seem likely that the transition corresponding to their indicated energy loss is really $(1s)^2-(2s)^2$. If the present calculations are at all correct it is much more likely this than $(1s)^2-(2p)^2$, although the possibility is not excluded that it may be $(1s)^2-(2s)(2p)$. Not until the total energy for the $(2s)(2p)$ is calculated can this point be decided.

In the $(1s)(2s)$ and $(1s)(2p)$ states since the $\epsilon$ value for the $(1s)$ in each case is much greater numerically than that for the 2-quantum electron, we may expect that the removal of the

[*] Cf. Hartree, reference 4, p. 95.

[8a] e.g. Bacher and Goudsmit, *Atomic Energy States*.

[9] R. Whiddington and H. Priestley, Proc. Roy. Soc. **A145**, 462 (1934).

TABLE II. *Contributions to Z of the various electrons in helium.*

| r | $(1s)^2$ (1s) | (1s)(2s) (1s) | (1s)(2s) (2s) | $(2s)^2$ (2s) | (2s)(2p) (2s) | (2s)(2p) (2p) | $(2p)^2$ (2p) | (1s)(2p) (1s) | (1s)(2p) (2p) |
|---|---|---|---|---|---|---|---|---|---|
| 0.00 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| .05 | .9992 | .9989 | .9999 | .9999 | .9999 | 1.0000 | 1.0000 | .9989 | 1.0000 |
| .10 | .9944 | .9922 | .9996 | .9993 | .9994 | 1.0000 | 1.0000 | .9921 | 1.0000 |
| .15 | .9836 | .9772 | .9989 | .9980 | .9983 | 1.0000 | 1.0000 | .9770 | 1.0000 |
| .20 | .9662 | .9533 | .9978 | .9958 | .9965 | 1.0000 | 1.0000 | .9527 | 1.0000 |
| .3 | .9131 | .8812 | .9945 | .9897 | .9914 | .9997 | 0.9998 | .8798 | 1.0000 |
| .4 | .8414 | .7862 | .9900 | .9823 | .9851 | .9990 | .9992 | .7838 | .9999 |
| .5 | .7590 | .6806 | .9853 | .9749 | .9790 | .9973 | .9979 | .6774 | .9998 |
| .6 | .6726 | .5744 | .9804 | .9688 | .9738 | .9943 | .9955 | .5706 | .9995 |
| .7 | .5875 | .4747 | .9761 | .9644 | .9700 | .9896 | .9918 | .4704 | .9990 |
| .8 | .5071 | .3854 | .9725 | .9618 | .9679 | .9826 | .9863 | .3810 | .9982 |
| .9 | .4332 | .3081 | .9698 | .9607 | .9669 | .9731 | .9787 | .3038 | .9971 |
| 1.0 | .3670 | .2432 | .9679 | .9605 | .9667 | .9610 | .9691 | .2392 | .9956 |
| 1.2 | .2579 | .1467 | .9661 | .9598 | .9662 | .9311 | .9429 | .1434 | .9909 |
| 1.4 | .1773 | .0854 | .9659 | .9542 | .9619 | .8876 | .9077 | .0831 | .9837 |
| 1.6 | .1197 | .0484 | .9655 | .9397 | .9502 | .8349 | .8644 | .0468 | .9735 |
| 1.8 | .0797 | .0269 | .9632 | .9141 | .9293 | .7755 | .8147 | .0258 | .9598 |
| 2.0 | .0525 | .0146 | .9575 | .8774 | .8987 | .7117 | .7603 | .0140 | .9426 |
| 2.2 | .0342 | .0079 | .9473 | .8310 | .8592 | .6461 | .7030 | .0075 | .9218 |
| 2.4 | .0221 | .0042 | .9321 | .7768 | .8123 | .5807 | .6446 | .0039 | .8974 |
| 2.6 | .0142 | .0022 | .9114 | .7175 | .7598 | .5173 | .5865 | .0021 | .8697 |
| 2.8 | .0091 | .0011 | .8856 | .6554 | .7037 | .4571 | .5298 | .0011 | .8391 |
| 3.0 | .0058 | .0006 | .8548 | .5923 | .6457 | .4011 | .4756 | .0006[b] | .8059 |
| 3.2 | .0036 | .0003 | .8198 | .5309 | .5875 | .3496 | .4243 | .0003 | .7705 |
| 3.4 | .0023 | .0002⁻ | .7812 | .4717 | .5304 | .3030 | .3765 | .0001 | .7335 |
| 3.6 | .0014 | .0001 | .7399 | .4159 | .4754 | .2611 | .3325 | .0001 | .6953 |
| 3.8 | .0009 | 0.0000 | .6966 | .3642 | .4234 | .2240 | .2922 | | .6564 |
| 4.0 | .0006 | | .6522 | .3170 | .3747 | .1913 | .2558 | | .6163 |
| 4.4 | .0002 | | .5625 | .2361 | .2888 | .1379 | .1937 | | .5393 |
| 4.8 | .0001 | | .4758 | .1725 | .2184 | .0981 | .1447 | | .4647 |
| 5.2 | | | .3955 | .1240 | .1624 | .0690 | .1068 | | .3951 |
| 5.6 | | | .3236 | .0878 | .1191 | .0480 | .0780 | | .3320 |
| 6.0 | | | .2611 | .0615 | .0862 | .0331 | .0564 | | .2758 |
| 6.8 | | | .1638 | .0292 | .0437 | .0154 | .0288 | | .1848 |
| 7.6 | | | .0985 | .0134 | .0214 | .0069 | .0143 | | .1193 |
| 8.4 | | | .0573 | .0060 | .0102 | .0031 | .0069 | | .0752 |
| 9.2 | | | .0323 | .0026 | .0047 | .0013 | .0033 | | .0460 |
| 10.0 | | | .0178 | .0011 | .0021 | .0006 | .0015 | | .0276 |
| 12 | | | .0037 | .0001 | .0003 | 0.0001 | .0002 | | .0071 |
| 14 | | | .0007 | | 0.0000 | 0.0000 | | | .0017 |
| 16 | | | 0.0001 | | | | | | .0004 |
| 18 | | | 0.0000 | | | | | | .0001 |
| 20 | | | | | | | | | |
| 22 | | | | | | | | | |

TABLE III. *Contributions to $Z_p$ of the various electrons in helium.*

| r | $(1s)^2$ (1s) | (1s)(2s) (1s) | (1s)(2s) (2s) | $(2s)^2$ (2s) | (2s)(2p) (2s) | (2s)(2p) (2p) | $(2p)^2$ (2p) | (1s)(2p) (1s) | (1s)(2p) (2p) |
|---|---|---|---|---|---|---|---|---|---|
| 0.00 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| .05 | .9161 | .9013 | .9850 | .9788 | .9804 | .9778 | .9793 | .9007 | .9873 |
| .10 | .8344 | .8057 | .9702 | .9580 | .9611 | .9555 | .9591 | .8046 | .9745 |
| .15 | .7564 | .7154 | .9556 | .9375 | .9422 | .9333 | .9386 | .7138 | .9618 |
| .20 | .6832 | .6314 | .9413 | .9176 | .9237 | .9110 | .9182 | .6295 | .9491 |
| .3 | .5522 | .4849 | .9137 | .8798 | .8883 | .8666 | .8773 | .4824 | .9236 |
| .4 | .4423 | .3667 | .8875 | .8442 | .8549 | .8223 | .8366 | .3640 | .8982 |
| .5 | .3530 | .2740 | .8624 | .8105 | .8231 | .7783 | .7960 | .2713 | .8727 |
| .6 | .2787 | .2027 | .8383 | .7783 | .7924 | .7348 | .7559 | .2002 | .8473 |
| .7 | .2198 | .1488 | .8150 | .7469 | .7625 | .6918 | .7162 | .1465 | .8220 |
| .8 | .1728 | .1084 | .7922 | .7160 | .7330 | .6498 | .6772 | .1065 | .7968 |
| .9 | .1356 | .0786 | .7699 | .6854 | .7037 | .6087 | .6390 | .0770 | .7717 |
| 1.0 | .1061 | .0566 | .7478 | .6548 | .6745 | .5688 | .6018 | .0553 | .7467 |
| 1.2 | .0647 | .0291 | .7039 | .5937 | .6161 | .4933 | .5306 | .0282 | .6973 |
| 1.4 | .0393 | .0147 | .6603 | .5330 | .5580 | .4241 | .4646 | .0142 | .6489 |
| 1.6 | .0237 | .0074 | .6166 | .4737 | .5010 | .3617 | .4041 | .0071 | .6017 |
| 1.8 | .0143 | .0037 | .5731 | .4169 | .4460 | .3064 | .3495 | .0035 | .5561 |
| 2.0 | .0086 | .0018 | .5300 | .3635 | .3938 | .2579 | .3007 | .0017 | .5121 |
| 2.2 | .0051 | .0009 | .4878 | .3143 | .3452 | .2159 | .2575 | .0008 | .4700 |
| 2.4 | .0031 | .0004 | .4466 | .2696 | .3005 | .1799 | .2196 | .0004 | .4300 |
| 2.6 | .0018 | .0002 | .4070 | .2297 | .2599 | .1492 | .1865 | .0002 | .3921 |
| 2.8 | .0011 | .0001 | .3691 | .1945 | .2236 | .1233 | .1579 | .0001 | .3560 |
| 3.0 | .0006 | .0000[b] | .3332 | .1638 | .1913 | .1016 | .1333 | .0000 | .3282 |
| 3.2 | .0004 | | .2996 | .1372 | .1629 | .0834 | .1121 | | .2921 |
| 3.4 | .0002 | | .2682 | .1144 | .1381 | .0683 | .0941 | | .2634 |
| 3.6 | .0001 | | .2392 | .0950 | .1167 | .0558 | .0788 | | .2369 |
| 3.8 | .0001 | | .2126 | .0786 | .0982 | .0454 | .0658 | | .2124 |
| 4.0 | .0000 | | .1882 | .0648 | .0823 | .0369 | .0549 | | .1900 |
| 4.4 | | | .1462 | .0437 | .0574 | .0243 | .0379 | | .1511 |
| 4.8 | | | .1122 | .0291 | .0395 | .0158 | .0260 | | .1191 |
| 5.2 | | | .0852 | .0192 | .0271 | .0103 | .0177 | | .0933 |
| 5.6 | | | .0641 | .0126 | .0184 | .0066 | .0120 | | .0724 |
| 6.0 | | | .0478 | .0082 | .0124 | .0042 | .0081 | | .0559 |
| 6.8 | | | .0260 | .0034 | .0055 | .0017 | .0036 | | .0327 |
| 7.6 | | | .0138 | .0014 | .0024 | .0007 | .0016 | | .0187 |
| 8.4 | | | .0071 | .0006 | .0011 | .0002 | .0007 | | .0105 |
| 9.2 | | | .0036 | .0003⁻ | .0005 | .0001 | .0003 | | .0058 |
| 10.0 | | | .0018 | .0001 | .0002 | | .0001 | | .0032 |
| 12 | | | .0003 | | .0000 | | .0000 | | .0007 |
| 14 | | | .0001⁻ | | | | | | .0001 |
| 16 | | | | | | | | | |
| 18 | | | | | | | | | |
| 20 | | | | | | | | | |

TABLE IV. *One-electron energy parameters.*

| STATE | ELECTRON | $-2\epsilon_0$ | $\epsilon$ CALC. | $\epsilon$ CALC. BY OTHER METHODS |
|---|---|---|---|---|
| $(1s)^2$ | (1s) | 3.374 | 1.836 | 1.809[a] |
| (1s)(2s) | (1s) | 3.972 | 3.469 | |
| | (2s) | 0.600 | 0.3058 | |
| $(2s)^2$ | (2s) | 0.950 | 0.4606 | 0.49[b] |
| (2s)(2p) | (2s) | 0.785 | 0.4195 | |
| | (2p) | 0.890 | 0.4443 | |
| $(2p)^2$ | (2p) | 0.818 | 0.3861 | |
| (1s)(2p) | (1s) | 3.995 | 3.496 | |
| | (2p) | 0.510 | 0.2522 | |

[a] E. A. Hylleraas, Zeits. f. Physik **65**, 209 (1930).
[b] F. G. Fender and J. P. Vinti, Phys. Rev. **46**, 78 (1934).

latter electron will not materially affect the wave function of the (1s) electron and hence the ionization energy to a fair approximation will be equal to the (2*s*) or (2*p*) value of $\epsilon$. We can then compare with the experimental values quoted by Bacher and Goudsmit (reference 8a, p. 220). They give 0.3506 for the (1*s*)(2*s*) $^3S$ and 0.2921 for (1*s*)(2*s*) $^1S$; the latter is in fair agreement with our computed value. The experimental value for (1*s*)(2*p*) $^3P$ is 0.2665 and that for (1*s*)(2*p*) $^1P$ is 0.2478; the latter again agrees fairly well with our 0.2522. In each case the agreement appears to

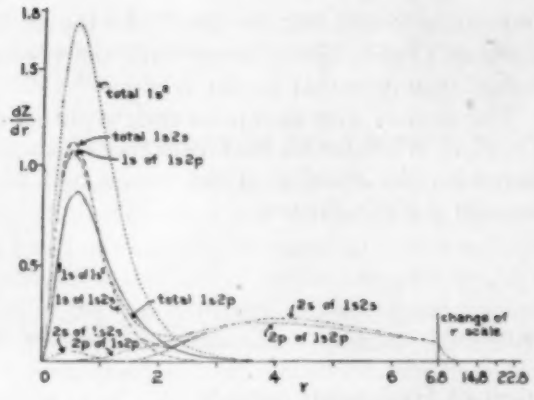


FIG. 2. Radial charge density for helium.

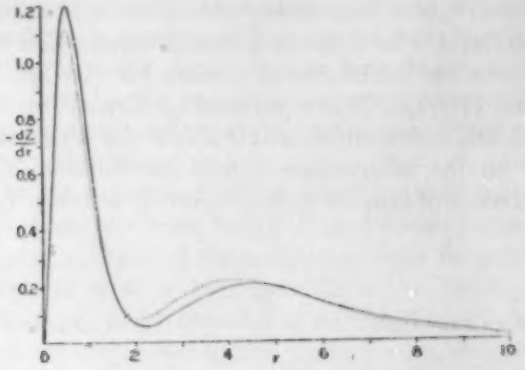


FIG. 4. Total radial charge density for He(1s)(2s). Solid line, Vinti; dotted line, present paper.

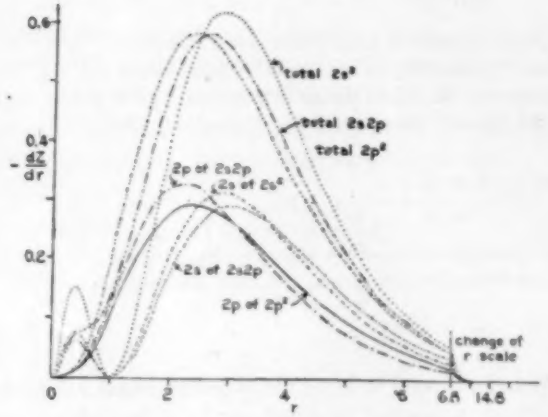


FIG. 3. Radial charge density for helium.

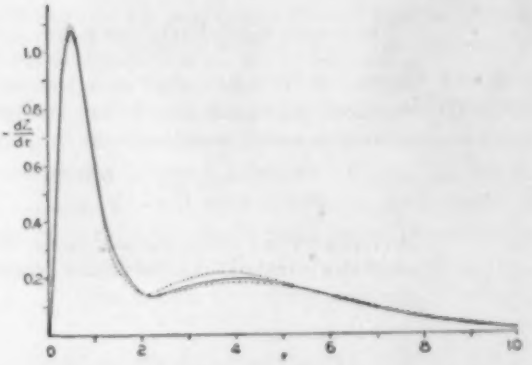


FIG. 5. Total radial charge density for He(1s)(2p). Solid line, present paper; dotted line, Eckart $(1s)(2p)^1p$; dash line, Eckart $(1s)(2p)^1p$.

be better with the singlet than with the triplet state. One might indeed expect that the self-consistent field value would agree better with some average of the singlet and triplet energies. It must be emphasized again, however, that the $\epsilon$ values are one-electron energy parameters only and further discussion of this question must await the calculation of the *total* energies of the various states. These are now under way and will be published shortly. It may be remarked that Hylleraas[10] has recently computed by the general method of his previous papers many discrete energy levels for singly excited helium, such as both the singlet and triplet terms of $(1s)(2s)$ and $(1s)(2p)$. He neglects the effect of the excitation on the inner electron. The agreement of his results with experiment is in general excellent.

[10] E. A. Hylleraas, Zeits. f. Physik **83**, 739 (1933).

In line with the procedure of some other writers, curves are presented (Figs. 2 and 3) exhibiting the radial charge density $-dZ/dr$ as a function of $r$ for the individual electrons as well as the completed group in the various states. These are self-explanatory and need no comment.

A further comparison of the results of the present calculations with those of other methods is suggested in connection with the radial charge density. Using a variational method Vinti[3] has found an analytic wave function for the $(1s)(2s)$ $^1S$ state. After the function has been suitably normalized to unity the radial charge density for the two electrons may be computed by multiplying the integral $2\int_0^\infty 4\pi r_2^2|\psi|^2 dr_2$ (a function of $r_1=r$) by $4\pi r^2$. The result is plotted in Fig. 4 and compared with $-dZ/dr$ for the corresponding case of the present paper. The agreement is

rather good considering the difference in the methods. Fig. 5 shows a similar comparison between the radial charge density for $(1s)(2p)\ ^1P$ and $(1s)(2p)\ ^3P$ as computed by Eckart[3] by the variational method and $-dZ/dr$ for this state from the self-consistent field calculations. The agreement is again seen to be very gratifying. It is interesting to note that the density for the singlet state of Eckart agrees better with the present values than does that for the triplet.

The authors wish to express their gratitude to Dr. F. E. White for his kind assistance in connection with the drawing of the curves and with some of the calculations.

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# The van der Waals Interaction of Hydrogen Atoms

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The van der Waals interaction energy of two hydrogen atoms at large internuclear distances is discussed by the use of a linear variation function. By including in the variation function, in addition to the unperturbed wave function, 26 terms for the dipole-dipole interaction, 17 for the dipole-quadrupole interaction, and 26 for the quadrupole-quadrupole interaction, the interaction energy is evaluated as

$$W''' = -\frac{6.49903\,e^2}{a_0\rho^6} - \frac{124.399\,e^2}{a_0\rho^8} - \frac{1135.21\,e^2}{a_0\rho^{10}} - \cdots,$$

in which $\rho = R/a_0$, with $R$ the internuclear distance. Some properties of the functions $F_{\nu\lambda\mu}(\xi, \vartheta, \varphi)$, which are orthogonal for the volume element $\xi d\xi \sin\vartheta d\vartheta d\varphi$, are discussed, and their usefulness in atomic problems is pointed out.

## INTRODUCTION

AN approximate second-order perturbation treatment of the inverse sixth power interaction energy of two hydrogen atoms a large distance apart (corresponding to the so-called dipole-dipole van der Waals attraction) was given in 1930 by Eisenschitz and London.[1] This treatment led to the result $W''' = -e^2 A/a_0\rho^6$, with $\rho = r_{AB}/a_0$ ($r_{AB}$ being the internuclear distance for the two atoms), $A$ being evaluated as 6.47. Applications of the variation method by Hassé[2] and by Slater and Kirkwood[3] verified this result essentially, the constant $A$ being shown to be equal to or greater than 6.4976.

As early as 1927 this problem had been attacked by Wang,[4] using the method developed by Epstein[5] for the treatment of the Stark effect. Wang claimed to have obtained an exact solution; it was, however, pointed out by Eisenschitz and London that Wang's result is necessarily in error. It seemed to us possible that Wang's work might have contained only a numerical error, and that the method might actually be capable of giving an exact solution. Because of the usefulness which a method of exact solution of problems of this sort would have, we thought it worth while to study the problem thoroughly. We have found that the method used by Wang does not give an exact solution,[6] but that it can be extended to give as closely approximate a solution as is desired. The results of the treatment are communicated in this paper.

A rough treatment of the dipole-quadrupole and quadrupole-quadrupole interactions of two hydrogen atoms has been published by Mar-

[1] R. Eisenschitz and F. London, Zeits. f. Physik **60**, 491 (1930).
[2] H. R. Hassé, Proc. Camb. Phil. Soc. **27**, 66 (1931).
[3] J. C. Slater and J. G. Kirkwood, Phys. Rev. **37**, 682 (1931).
[4] S. C. Wang, Physik. Zeits. **28**, 663 (1927).
[5] P. S. Epstein, Phys. Rev. **28**, 695 (1926).

[6] Wang does not present the final steps in his calculation in detail, but states that he set up a sixth degree secular equation from which he obtained an accurate value for the energy. We believe that the error in his treatment occurs at this point.

genau.[7] We have applied our method to obtain reasonably accurate expressions for these interactions also.

## Formulation of the Problem

In the wave equation for two hydrogen atoms $H\psi=W\psi$ let us put $H=H^0+H'$, $H^0$ being the part of the Hamiltonian corresponding to two isolated hydrogen atoms and $H'$ representing the interaction of the two hydrogen atoms. In order to do this we neglect the resonance phenomenon (which is unimportant at large distances), taking as the unperturbed wave function the product function $\psi_{100}(A1)\ \psi_{100}(B2)$; that is, we consider electron 1 to be attached to nucleus $A$ and electron 2 to nucleus $B$. We also write $W=W^0+W''$ ($W'$, the first-order perturbation energy, being equal to zero). We shall consider only the interaction of two normal hydrogen atoms, so that $W^0$ is equal to $-e^2/a_0$. Making the substitutions $\xi_1=2r_{A1}/a_0$ and $\xi_2=2r_{B2}/a_0$, the wave equation becomes

$$\left(\nabla_1^2+\frac{1}{\xi_1}-\frac{1}{4}\right)\psi+\left(\nabla_2^2+\frac{1}{\xi_2}-\frac{1}{4}\right)\psi-\frac{a_0}{2e^2}H'\psi=\lambda\psi, \quad (1)$$

in which $\lambda=-W''a_0/2e^2$.

The interaction $H'$ is equal to

$$-e^2/r_{A2}-e^2/r_{B1}+e^2/r_{AB}+e^2/r_{12}.$$

If $R(=r_{AB})$ is large, this can be expanded[7] in inverse powers of $R$ to give the expression

$$\begin{aligned}H'=&(e^2/R^3)(x_1x_2+y_1y_2-2z_1z_2)\\&+(3/2)(e^2/R^4)\{r_1^2z_2-r_2^2z_1\\&+(2x_1x_2+2y_1y_2-3z_1z_2)(z_1-z_2)\}\\&+\tfrac{3}{4}(e^2/R^5)\{r_1^2r_2^2-5r_2^2z_1^2-5r_1^2z_2^2\\&-15z_1^2z_2^2+2(x_1x_2+y_1y_2+4z_1z_2)^2\}+\cdots. \quad (2)\end{aligned}$$

In this expression $x_1y_1z_1$ are Cartesian coordinates of electron 1 relative to nucleus $A$, and $x_2y_2z_2$ those of electron 2 relative to nucleus $B$, the $z$ axis for each being directed towards the other nucleus. The first term represents the mutual energy of two dipoles; this term alone is important for large values of $R$. The second and third terms represent the dipole-quadrupole and quadrupole-quadrupole interactions, respectively. It can be easily shown that in the calculation of the second-order perturbation energy the terms can be considered separately, their contributions being additive.

In the solution of the problem we shall make use of the functions $F_{\nu\lambda\mu}(\xi, \vartheta, \varphi)$ discussed in the appendix. Each of these functions can be made identical with a hydrogen-like wave function $\psi_{nlm}(r, \vartheta, \varphi)$ by choosing a suitable linear relation between $r$ and $\xi$; the functions $F_{\nu\lambda\mu}$ all contain the same exponential function, in contradistinction to the functions $\psi_{nlm}$. We have defined $\xi_1$ and $\xi_2$ in such a way that $F_{100}(\xi_1, \vartheta_1, \varphi_1)$ and $F_{100}(\xi_2, \vartheta_2, \varphi_2)$ are identical with $\psi_{100}(r_1, \vartheta_1, \varphi_1)$ and $\psi_{100}(r_2, \vartheta_2, \varphi_2)$, respectively; that is, the unperturbed wave function can be written as $F_{100}(\xi_1)\ F_{100}(\xi_2)$. We now apply the variation method in treating the perturbed wave equation, using as the variation function a linear combination of the product functions $F_{\nu_1\lambda_1\mu_1}(\xi_1, \vartheta_1, \varphi_1)$ $F_{\nu_2\lambda_2\mu_2}(\xi_2, \vartheta_2, \varphi_2)$, with arbitrary coefficients. It can be seen that the second-order perturbation energy for the perturbation function

$$\begin{aligned}H'=&-(2e^2/a_0)\{\alpha\xi_1\xi_2\cos\vartheta_1\cos\vartheta_2\\&+\beta\xi_1\xi_2^2\cos\vartheta_1(3\cos^2\vartheta_2-1)\\&+\gamma\xi_1^2\xi_2^2(3\cos^2\vartheta_1-1)(3\cos^2\vartheta_2-1)\\&+\cdots\}, \quad (3)\end{aligned}$$

in which

$$\alpha=(6)!a_0^3/8R^3, \quad \beta=(30)!a_0^4/32R^4,$$
$$\text{and} \quad \gamma=(70)!a_0^5/128R^5, \quad (4)$$

is identical with that for the function of Eq. (2), and, moreover, that to obtain the first-order perturbed wave function and the second-order perturbation energy, the variation function used need contain, in addition to the unperturbed part $F_{100}(\xi_1)\ F_{100}(\xi_2)$, only the terms $F_{\nu_1 10}(\xi_1, \vartheta_1)$ $F_{\nu_2 10}(\xi_2, \vartheta_2)$ (for the dipole-dipole term in $\alpha$), $F_{\nu_1 10}(\xi_1, \vartheta_1)\ F_{\nu_2 20}(\xi_2, \vartheta_2)$ (for the term in $\beta$), and $F_{\nu_1 20}(\xi_1, \vartheta_1)$. $F_{\nu_2 20}(\xi_2, \vartheta_2)$ (for the term in $\gamma$).[8]

[7] H. Margenau, Phys. Rev. **38**, 747 (1931).

[8] On application of the ordinary methods of perturbation theory, it is seen that the first-order perturbed wave function for a normal hydrogen atom with perturbation function $f(r)T(\vartheta, \varphi)$, where $T$ is a tesseral harmonic, has the form $\Psi_{100}(r)+\Phi(r)T(\vartheta, \varphi)$, the perturbed part involving the same tesseral harmonic as the perturbation function. The statements in the text can be verified by an extension of this argument.

For a linear variation function $\sum_i a_i\Phi_i$ (where $\Phi_i$ represents the product functions $F_{\nu_1\lambda_1\mu_1}(\xi_1, \vartheta_1, \varphi_1)\, F_{\nu_2\lambda_2\mu_2}(\xi_2, \vartheta_2, \varphi_2)$) the secular equation corresponding to the wave equation (1) is the determinantal equation[9]

$$|\mathcal{H}_{jk}^0+\mathcal{H}_{jk}'-\Delta_{jk}\lambda| = 0, \qquad (5)$$

in which

$$\mathcal{H}_{jk}^0 = \int\int \Phi_j^*(\nabla_1^2+(1/\xi_1)-\tfrac{1}{4} +\nabla_2^2+(1/\xi_2)-\tfrac{1}{4})\Phi_k d\tau_1 d\tau_2,$$

$$\mathcal{H}_{jk}' = \int\int \Phi_j^*(-(a_0/2e^2)H')\Phi_k d\tau_1 d\tau_2,$$

and

$$\Delta_{jk} = \int\int \Phi_j^*\Phi_k d\tau_1 d\tau_2,$$

$d\tau_1$ being equal to $\xi_1^2 \sin\theta_1 d\xi_1 d\vartheta_1 d\varphi_1$ (with $d\tau_2$ differing only in the subscripts) and the integrals extending over the configuration space of the system. It is to be noted that the volume element $d\tau_1 d\tau_2$ is not such as to make the functions $\Phi$ mutually orthogonal. The integrals can be evaluated with the help of the relations given in the appendix. To obtain the second-order perturbation energy we need introduce the term in $\lambda$ in the row and column corresponding to the wave function for the unperturbed system only.

## The Dipole-Dipole Interaction

The secular equation for the dipole-dipole interaction is

| $\nu_1\lambda_1\mu_1\nu_2\lambda_2\mu_2$ | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 100100 | $-4\lambda$ | $32\alpha$ | $-16\alpha$ | $-16\alpha$ | $8\alpha$ | 0 | 0 | 0 | 0 | 0 | ⋯ | |
| 210210 | $32\alpha$ | $-8$ | 2 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | ⋯ | |
| 210310 | $-16\alpha$ | 2 | $-14$ | 0 | 4 | $\sqrt{(10)}$ | 0 | 0 | 0 | 0 | ⋯ | |
| 310210 | $-16\alpha$ | 2 | 0 | $-14$ | 4 | 0 | $\sqrt{(10)}$ | 0 | 0 | 0 | ⋯ | |
| 310310 | $8\alpha$ | 0 | 4 | 4 | $-24$ | 0 | 0 | $2\sqrt{(10)}$ | $2\sqrt{(10)}$ | 0 | ⋯ | |
| 210410 | 0 | 0 | $\sqrt{(10)}$ | 0 | 0 | $-20$ | 0 | 6 | 0 | 0 | ⋯ | |
| 410210 | 0 | 0 | 0 | $\sqrt{(10)}$ | 0 | 0 | $-20$ | 0 | 6 | 0 | ⋯ | $=0, \quad (6)$ |
| 310410 | 0 | 0 | 0 | 0 | $2\sqrt{(10)}$ | 6 | 0 | $-34$ | 0 | $3\sqrt{(10)}$ | ⋯ | |
| 410310 | 0 | 0 | 0 | 0 | $2\sqrt{(10)}$ | 0 | 6 | 0 | $-34$ | $3\sqrt{(10)}$ | ⋯ | |
| 410410 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | $3\sqrt{(10)}$ | $3\sqrt{(10)}$ | $-48$ | ⋯ | |
| . | . | . | . | . | . | . | . | . | . | . | | |
| . | . | . | . | . | . | . | . | . | . | . | | |
| . | . | . | . | . | . | . | . | . | . | . | | |

the rows and columns corresponding to the values of $\nu_1 \cdots \mu_2$ shown at the left. We obtain successive approximations to the solution of this equation by neglecting rows and columns beyond the $n$th. This process has been carried out for $n = 2, 5, 10, 17$ and 26. Some simplification is achieved by combining rows (and columns) with $\nu_1$ and $\nu_2$ interchanged, the corresponding functions having the same coefficient. The results of the calculation are given in Table I, in terms of the constant $A$ in the expression $W'' = -Ae^2/a_0\rho^6$, with $\rho = R/a_0$ ($A$ being equal to $3\lambda/16\alpha^2$).

Table I. *The dipole-dipole interaction constant A.*

| Degree of approx. | Terms included | | $A$ |
|---|---|---|---|
| 2 | $\nu_1 \leq 2$, | $\nu_2 \leq 2$ | 6 |
| 5 | 3 | 3 | 6.4822 |
| 10 | 4 | 4 | 6.4984 |
| 17 | 5 | 5 | 6.49899 |
| 26 | 6 | 6 | 6.49903 |

Table II. *The dipole-quadrupole interaction constant B.*

| Degree of approx. | Terms included | | $B$ |
|---|---|---|---|
| 2 | $\nu_1 \leq 2$, | $\nu_2 \leq 3$ | 115.7 |
| 5 | 3 | 4 | 124.10 |
| 10 | 4 | 5 | 124.386 |
| 17 | 5 | 6 | 124.399 |

Table III. *The quadrupole-quadrupole interaction constant C.*

| Degree of approx. | Terms included | | $C$ |
|---|---|---|---|
| 2 | $\nu_1 \leq 3$, | $\nu_2 \leq 3$ | 1063.1 |
| 5 | 4 | 4 | 1132.6 |
| 10 | 5 | 5 | 1134.35 |
| 17 | 6 | 6 | 1135.12 |
| 26 | 7 | 7 | 1135.21 |

It is seen that the convergence is rapid, the final value of $A$, 6.49903, being trustworthy to within one unit in the last decimal place.

[9] See, for example, L. Pauling and E. B. Wilson, Jr., *Introduction to Quantum Mechanics, with Applications to Chemistry*, McGraw-Hill Book Co., 1935, Chap. VII.

### The Dipole-Quadrupole Interaction

The secular equation for the dipole-quadrupole interaction is

| $\nu_1\lambda_1\mu_1\nu_2\lambda_2\mu_2$ | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 100100 | $-4\lambda$ | $-192\sqrt{(3)}\beta$ | $96\sqrt{(3)}\beta$ | $96\sqrt{2}\beta$ | $-48\sqrt{2}\beta$ | 0 | 0 | 0 | 0 | 0 | ⋯ | |
| 210320 | $-192\sqrt{(3)}\beta$ | $-14$ | 4 | $\sqrt{(6)}$ | 0 | 0 | 0 | 0 | 0 | 0 | ⋯ | |
| 310320 | $96\sqrt{(3)}\beta$ | 4 | $-24$ | 0 | $2\sqrt{(6)}$ | $2\sqrt{(10)}$ | 0 | 0 | 0 | 0 | ⋯ | |
| 210420 | $96\sqrt{2}\beta$ | $\sqrt{(6)}$ | 0 | $-20$ | 6 | 0 | $\sqrt{(14)}$ | 0 | 0 | 0 | ⋯ | |
| 310420 | $-48\sqrt{2}\beta$ | 0 | $2\sqrt{(6)}$ | 6 | $-34$ | 0 | 0 | $3\sqrt{(10)}$ | $2\sqrt{(14)}$ | 0 | ⋯ | |
| 410320 | 0 | 0 | $2\sqrt{(10)}$ | 0 | 0 | $-34$ | 0 | $3\sqrt{(6)}$ | 0 | 0 | ⋯ | |
| 210520 | 0 | 0 | 0 | $\sqrt{(14)}$ | 0 | 0 | $-26$ | 0 | 8 | 0 | ⋯ | $=0.$ (7) |
| 410420 | 0 | 0 | 0 | 0 | $3\sqrt{(10)}$ | $3\sqrt{(6)}$ | 0 | $-48$ | 0 | $3\sqrt{(14)}$ | ⋯ | |
| 310520 | 0 | 0 | 0 | 0 | $2\sqrt{(14)}$ | 0 | 8 | 0 | $-44$ | $4\sqrt{(10)}$ | ⋯ | |
| 410520 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | $3\sqrt{(14)}$ | $4\sqrt{(10)}$ | $-62$ | ⋯ | |
| . | . | . | . | . | . | . | . | . | . | . | | |
| . | . | . | . | . | . | . | . | . | . | . | | |
| . | . | . | . | . | . | . | . | . | . | . | | |

We have solved this equation approximately, the results being given in Table II in terms of the constant $B$ in the energy expression $-Be^2/a_0\rho^5$.

The error in the final value of $B$ we estimate to be less than one unit in the last figure quoted.

### The Quadrupole-Quadrupole Interaction

The secular equation for the quadrupole-quadrupole interaction is

| $\nu_1\lambda_1\mu_1\nu_2\lambda_2\mu_2$ | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 100100 | $-4\lambda$ | $3456\gamma$ | $-576\sqrt{(6)}\gamma$ | $-576\sqrt{(6)}\gamma$ | $576\gamma$ | 0 | 0 | 0 | 0 | 0 | ⋯ | |
| 320320 | $3456\gamma$ | $-24$ | $2\sqrt{(6)}$ | $2\sqrt{(6)}$ | 0 | 0 | 0 | 0 | 0 | 0 | ⋯ | |
| 320420 | $-576\sqrt{(6)}\gamma$ | $2\sqrt{(6)}$ | $-34$ | 0 | $3\sqrt{(6)}$ | $2\sqrt{(14)}$ | 0 | 0 | 0 | 0 | ⋯ | |
| 420320 | $-576\sqrt{(6)}\gamma$ | $2\sqrt{(6)}$ | 0 | $-34$ | $3\sqrt{(6)}$ | 0 | $2\sqrt{(14)}$ | 0 | 0 | 0 | ⋯ | |
| 420420 | $576\gamma$ | 0 | $3\sqrt{(6)}$ | $3\sqrt{(6)}$ | $-48$ | 0 | 0 | $3\sqrt{(14)}$ | $3\sqrt{(14)}$ | 0 | ⋯ | |
| 320520 | 0 | 0 | $2\sqrt{(14)}$ | 0 | 0 | $-44$ | 0 | $4\sqrt{(6)}$ | 0 | 0 | ⋯ | |
| 520320 | 0 | 0 | 0 | $2\sqrt{(14)}$ | 0 | 0 | $-44$ | 0 | $4\sqrt{(6)}$ | 0 | ⋯ | $=0.$ (8) |
| 420520 | 0 | 0 | 0 | 0 | $3\sqrt{(14)}$ | $4\sqrt{(6)}$ | 0 | $-62$ | 0 | $4\sqrt{(14)}$ | ⋯ | |
| 520420 | 0 | 0 | 0 | 0 | $3\sqrt{(14)}$ | 0 | $4\sqrt{(6)}$ | 0 | $-62$ | $4\sqrt{(14)}$ | ⋯ | |
| 520520 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | $4\sqrt{(14)}$ | $4\sqrt{(14)}$ | $-80$ | ⋯ | |
| . | . | . | . | . | . | . | . | . | . | . | | |
| . | . | . | . | . | . | . | . | . | . | . | | |
| . | . | . | . | . | . | . | . | . | . | . | | |

The results of the approximate solution of this equation, in terms of the constant $C$ in the energy expression $-Ce^2/a_0\rho^{10}$, are given in Table III.

The final value, $C=1135.21$, is reliable except for the last figure.

### Discussion of Results

We have thus found for the interaction energy of two normal hydrogen atoms at the large distance $R=\rho a_0$ the expression

$$W''=-\frac{6.49903\,e^2}{a_0\rho^6}-\frac{124.399\,e^2}{a_0\rho^8}-\frac{1135.21\,e^2}{a_0\rho^{10}}-\cdots. \tag{9}$$

It is interesting to note that the value $A=6.4976$ found by Hassé for the dipole-dipole coefficient by the use of a variation function $\psi_{100}(r_1)\,\psi_{100}(r_2)\,\{1+H'(A+Br_1r_2+Cr_1^2r_2^2+Dr_1^3r_2^3)\}$ is very close to our value for $\nu_1\leq 4$, $\nu_2\leq 4$, which is based on a variation function involving all terms (unsymmetric as well as symmetric) out to $r_1^3r_2^3$. This indicates that the unsymmetric terms are of minor importance.

[10] We use here shortened symbols, such as $F_{\nu_1}F_{\nu_2}$ for $F_{\nu_1\lambda_1\mu_1}(\xi_1,\vartheta_1,\varphi_1)F_{\nu_2\lambda_2\mu_2}(\xi_2,\vartheta_2,\varphi_2)$, etc.

The approximate second-order perturbation energy $W_0''=(H_{00}')^2/W_0^0$, with $W_0^0=-e^2/a_0$, leads to the values $A=6$, $B=135$, and $C=1417.5$, the last two values being given by Margenau.[7] It is seen that the value of $A$ is too low, and those of $B$ and $C$ are too high. This means that the dipole-dipole interaction is due more to excited states with negative energy (less than $e^2/a_0$ above the normal state of the system of two hydrogen atoms) than to excited states with positive energy, whereas the dipole-quadrupole and quadrupole-quadrupole interactions are due more to the latter than to the former states.

As has been pointed out by earlier authors, the van der Waals forces are more important than exchange forces for values of $R$ greater than about $7a_0$. At this distance the dipole-quadrupole force is about one-half as large as the dipole-dipole force, and the quadrupole-quadrupole force is about one-eighth as large, the dipole-dipole attraction becoming relatively still more important at larger distances. This van der Waals calculation, based on product wave functions, is not significant for values of $R$ much less than $7a_0$ because of neglect of the resonance phenomenon and because of failure of the expansion given in Eq. (2).

While our treatment has not led to an exact solution of our problem, the use of the functions $F_{\nu\lambda\mu}(\xi, \vartheta, \varphi)$ has permitted the reasonably accurate approximate solution to be made with considerable ease, and we feel that these functions may be found useful in the treatment of other problems of atomic and molecular structure.[11]

## Appendix

### The functions $F_{\nu\lambda\mu}(\xi, \vartheta, \varphi)$

We define

$$F_{\nu\lambda\mu}(\xi, \vartheta, \varphi)=\Lambda_{\nu\lambda}(\xi)\Theta_{\lambda\mu}(\vartheta)\Phi_\mu(\varphi),$$

with

$$\Lambda_{\nu\lambda}(\xi)=\{(\nu-\lambda-1)!/[(\nu+\lambda)!]^3\}^{\frac{1}{2}}e^{-\xi/2}\xi^\lambda L_{\nu+\lambda}^{2\lambda+1}(\xi),$$

$L$ being an associated Laguerre polynomial,

$$\Theta_{\lambda\mu}(\vartheta)=\{[(2\lambda+1)(\lambda-\mu)!]/2(\lambda+\mu)!\}^{\frac{1}{2}}P_\lambda^{|\mu|}(\cos\vartheta),$$

$P$ being an associated Legendre function, and

$$\Phi_\mu(\varphi)=(2\pi)^{-\frac{1}{2}}e^{i\mu\varphi}.$$

The functions are orthogonal and normalized for the weight function $\xi\sin\vartheta$, satisfying the equation

$$\int_0^\infty\int_0^\pi\int_0^{2\pi}F'_{\nu'\lambda'\mu'}(\xi, \vartheta, \varphi)F_{\nu\lambda\mu}(\xi, \vartheta, \varphi)\xi\sin\vartheta\,d\varphi\,d\vartheta\,d\xi=\delta_{\nu'\nu}\delta_{\lambda'\lambda}\delta_{\mu'\mu}.$$

$F_{\nu\lambda\mu}(\xi, \vartheta, \varphi)$ satisfies the differential equation

$$(\nabla^2+1/\xi-\tfrac{1}{4})F_{\nu\lambda\mu}=-[(\nu-1)/\xi]F_{\nu\lambda\mu}.$$

The following relations involving the $\Lambda$'s can be easily derived from the properties of the associated Laguerre polynomials:

$$\xi\Lambda_{\nu\lambda}=-\{(\nu-\lambda)(\nu+\lambda+1)\}^{\frac{1}{2}}\Lambda_{\nu+1,\,\lambda}+2\nu\Lambda_{\nu\lambda}-\{(\nu+\lambda)(\nu-\lambda-1)\}^{\frac{1}{2}}\Lambda_{\nu-1,\,\lambda},$$

$$\begin{aligned}\xi^2\Lambda_{\nu\lambda}=&-\{(\nu-\lambda)(\nu+\lambda+1)(\nu+\lambda+2)(\nu+\lambda+3)\}^{\frac{1}{2}}\Lambda_{\nu+2,\,\lambda+1}\\&+2(2\nu-\lambda)\{(\nu+\lambda+1)(\nu+\lambda+2)\}^{\frac{1}{2}}\Lambda_{\nu+1,\,\lambda+1}-6\nu\{(\nu+\lambda+1)(\nu-\lambda-1)\}^{\frac{1}{2}}\Lambda_{\nu,\,\lambda+1}\\&+2(2\nu+\lambda)\{(\nu-\lambda-1)(\nu-\lambda-2)\}^{\frac{1}{2}}\Lambda_{\nu-1,\,\lambda+1}-\{(\nu+\lambda)(\nu-\lambda-1)(\nu-\lambda-2)(\nu-\lambda-3)\}^{\frac{1}{2}}\Lambda_{\nu-2,\,\lambda+1}.\end{aligned}$$

[11] *Added in proof:* Professor J. H. Van Vleck has pointed out to us that the functions were used in the treatment of dispersion by hydrogen-like atoms by B. Podolsky, Proc. Nat. Acad. Sci. **14**, 253 (1928).

$$\begin{aligned}\xi^2\Lambda_{\nu\lambda}=&-\{(\nu-\lambda)(\nu+\lambda+1)(\nu+\lambda+2)(\nu+\lambda+3)(\nu+\lambda+4)(\nu+\lambda+5)\}^{\frac{1}{2}}\Lambda_{\nu+3,\,\lambda+2}\\&+2(3\nu-2\lambda)\{(\nu+\lambda+1)(\nu+\lambda+2)(\nu+\lambda+3)(\nu+\lambda+4)\}^{\frac{1}{2}}\Lambda_{\nu+2,\,\lambda+2}\\&-5(3\nu-\lambda)\{(\nu-\lambda-1)(\nu+\lambda+1)(\nu+\lambda+2)(\nu+\lambda+3)\}^{\frac{1}{2}}\Lambda_{\nu+1,\,\lambda+2}\\&+20\nu\{(\nu+\lambda+1)(\nu+\lambda+2)(\nu-\lambda-1)(\nu-\lambda-2)\}^{\frac{1}{2}}\Lambda_{\nu,\,\lambda+2}\\&-5(3\nu+\lambda)\{(\nu+\lambda+1)(\nu-\lambda-1)(\nu-\lambda-2)(\nu-\lambda-3)\}^{\frac{1}{2}}\Lambda_{\nu-1,\,\lambda+2}\\&+2(3\nu+2\lambda)\{(\nu-\lambda-1)(\nu-\lambda-2)(\nu-\lambda-3)(\nu-\lambda-4)\}^{\frac{1}{2}}\Lambda_{\nu-2,\,\lambda+2}\\&-\{(\nu+\lambda)(\nu-\lambda-1)(\nu-\lambda-2)(\nu-\lambda-3)(\nu-\lambda-4)(\nu-\lambda-5)\}^{\frac{1}{2}}\Lambda_{\nu-3,\,\lambda+2}.\end{aligned}$$

From these we obtain similar relations in the $F$'s. The following special cases are needed in evaluating the matrix elements in Eqs. (6), (7) and (8):

$$\xi F_{100}=-\sqrt{2}F_{200}+2F_{100},$$

$$\xi^2\cos\vartheta F_{100}=-2\sqrt{2}F_{310}+4\sqrt{2}F_{210},$$

$$\xi^3(3\cos^2\vartheta-1)F_{100}=-24F_{420}+24\sqrt{(6)}F_{320}.$$

**The evaluation of the matrix elements**

In order to illustrate the method of construction of the matrices in Eqs. (6), (7) and (8), we shall evaluate some of the integrals. Let us first consider the integral[10]

$$\mathfrak{K}^0_{\nu_1'\nu_2'\nu_1\nu_2}=\int\int F^*_{\nu_1'}F^*_{\nu_2'}\{\nabla_1^2+1/\xi_1-\tfrac{1}{4}+\nabla_2^2+1/\xi_2-\tfrac{1}{4}\}F_{\nu_1}F_{\nu_2}d\tau_1d\tau_2.$$

By using the differential equation for $F_{\nu\lambda\mu}(\xi,\vartheta,\varphi)$, the equation becomes

$$\begin{aligned}\mathfrak{K}^0_{\nu_1'\nu_2'\nu_1\nu_2}&=\int\cdots\int F^*_{\nu_1'}F^*_{\nu_2'}\{-(\nu_1-1)/\xi_1-(\nu_2-1)/\xi_2\}F_{\nu_1}F_{\nu_2}\xi_1^2\xi_2^2\sin\vartheta_1\sin\vartheta_2d\xi_1d\vartheta_1d\varphi_1d\xi_2d\vartheta_2d\varphi_2\\&=\int\cdots\int F^*_{\nu_1'}F^*_{\nu_2'}\{-(\nu_1-1)\xi_2-(\nu_2-1)\xi_1\}F\nu_1F_{\nu_2}\xi_1\xi_2\sin\theta_1\sin\theta_2d\xi_1d\vartheta_1d\varphi_1d\xi_2d\vartheta_2d\varphi_2.\end{aligned}$$

For Eq. (6) ($\lambda_1=\lambda_2=1$, $\mu_1=\mu_2=0$) this becomes

$$\begin{aligned}\mathfrak{K}^0_{\nu_1'\nu_2'\nu_1\nu_2}=\int\cdots\int F^*_{\nu_1'}F^*_{\nu_2'}&[(\nu_2-1)\{(\nu_1-1)(\nu_1+2)\}^{\frac{1}{2}}F_{\nu_1+1}F_{\nu_2}+(\nu_1-1)\{(\nu_2-1)(\nu_2+2)\}^{\frac{1}{2}}F_{\nu_1}F_{\nu_2+1}\\&-2(2\nu_1\nu_2-\nu_1-\nu_2)F_{\nu_1}F_{\nu_2}+(\nu_2-1)\{(\nu_1+1)(\nu_1-2)\}^{\frac{1}{2}}F_{\nu_1-1}F_{\nu_2}\\&+(\nu_1-1)\{(\nu_2+1)(\nu_2-2)\}^{\frac{1}{2}}F_{\nu_1}F_{\nu_2-1}]\xi_1\xi_2\sin\vartheta_1\sin\vartheta_2d\xi_1d\vartheta_1d\varphi_1d\xi_2d\vartheta_2d\varphi_2.\end{aligned}$$

and hence we obtain

$$\mathfrak{K}^0_{\nu_1+1,\,\nu_2,\,\nu_1,\,\nu_2}=(\nu_2-1)\{(\nu_1-1)(\nu_1+2)\}^{\frac{1}{2}},$$

$$\mathfrak{K}^0_{\nu_1,\,\nu_2+1,\,\nu_1,\,\nu_2}=(\nu_1-1)\{(\nu_2-1)(\nu_2+2)\}^{\frac{1}{2}},$$

$$\mathfrak{K}^0_{\nu_1-1,\,\nu_2,\,\nu_1,\,\nu_2}=(\nu_2-1)\{(\nu_1+1)(\nu_1-2)\}^{\frac{1}{2}},$$

$$\mathfrak{K}^0_{\nu_1,\,\nu_2-1,\,\nu_1,\,\nu_2}=(\nu_1-1)\{(\nu_2+1)(\nu_2-2)\}^{\frac{1}{2}},$$

and

$$\mathfrak{K}^0_{\nu_1,\,\nu_2,\,\nu_1,\,\nu_2}=-2(2\nu_1\nu_2-\nu_1-\nu_2),$$

all others being equal to zero.

In Eq. (7) we have

$$\mathcal{K}'_{\nu_1\nu_2,\,11}=\beta\int\cdots\int F_{\nu_1}^{*}F_{\nu_2}^{*}\xi_1\xi_2^2\cos\vartheta_1(3\cos^2\vartheta_2-1)F_1F_1\xi_1^2\xi_2^2\sin\vartheta_1\sin\vartheta_2 d\xi_1 d\vartheta_1 d\varphi_1 d\xi_2 d\vartheta_2 d\varphi_2$$

$$=\beta\int\cdots\int F_{\nu_1}^{*}F_{\nu_2}^{*}\{48\sqrt{2}F_{310}F_{420}-96\sqrt{(3)}F_{310}F_{320}-96\sqrt{2}F_{210}F_{420}$$

$$+192\sqrt{(3)}F_{210}F_{320}\}\xi_1\xi_2\sin\vartheta_1\sin\vartheta_2 d\xi_1 d\vartheta_1 d\varphi_1 d\xi_2 d\vartheta_2 d\varphi_2,$$

and hence

$$\mathcal{K}'_{23,11}=192\sqrt{(3)}\beta,\qquad \mathcal{K}'_{33,11}=-96\sqrt{(3)}\beta,\qquad \mathcal{K}'_{24,11}=-96\sqrt{2}\beta,$$

and $\mathcal{K}'_{24,\,11}=48\sqrt{2}\beta$, all others being equal to zero.

To illustrate the evaluation of the integral $\Delta$ let us consider $\Delta_{11,\,11}$:

$$\Delta_{11,\,11}=\int\cdots\int\{F_{100}(\xi_1)F_{100}(\xi_2)\}^2\xi_1^2\xi_2^2\sin\vartheta_1\sin\vartheta_2 d\xi_1 d\vartheta_1 d\varphi_1 d\xi_2 d\vartheta_2 d\varphi_2$$

$$=\int\cdots\int F_{100}(\xi_1)F_{100}(\xi_2)\{2F_{200}(\xi_1)F_{200}(\xi_2)-2\sqrt{2}F_{200}(\xi_1)F_{100}(\xi_2)-2\sqrt{2}F_{100}(\xi_1)F_{200}(\xi_2)$$

$$+4F_{100}(\xi_1)F_{100}(\xi_2)\}\xi_1\xi_2\sin\vartheta_1\sin\vartheta_2 d\xi_1 d\vartheta_1 d\varphi_1 d\xi_2 d\vartheta_2 d\varphi_2,$$

or, making use of the orthogonality and normalization of the $F$'s, $\Delta_{11,\,11}=4$.

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# The Magnetic Moment of the $K^{39}$ Nucleus

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Starting with the $K^+$ field given by Hartree, a 4*s* wave function has been found by numerical integration. The orthogonality correction diminishes the value of the wave function at the origin by about one-third. The experimental value of the hyperfine structure separation of the $^2S$ normal state is 0.015 $cm^{-1}$. From this is calculated a molecular magnetic moment of 1.2 nuclear magnetons, as compared with the value of 0.38 nuclear magnetons calculated by Millman, Fox and Rabi on the basis of the modified Goudsmit's formula. The disagreement seems to be due chiefly to the possibility that the single electron wave functions of Fermi and Segré are not mutually orthogonal.

THERE have recently been published two independent determinations of the h.f.s. separation of the normal state of the $K^{39}$ atom. Jackson and Kuhn[1] have used a spectroscopic method; Millman, Fox and Rabi[2] have relied on the method of molecular beams. The numerical agreement is good, and 0.015 $cm^{-1}$ may be taken as the value of the separation.

From this, Millman, Fox and Rabi estimate the value of the nuclear magnetic moment to be 0.38 nuclear magneton, using the semi-empirical formula due to Goudsmit[3] and Fermi and Segré.[4, 5] Since previous cases of low magnetic moments have been associated with isotopes of even mass number, the above value seemed somewhat anomalous, and we therefore thought it of interest to ascertain whether or not the "anomaly" could be removed by the use of a Hartree wave function. This we now proceed to investigate.

[1] D. A. Jackson and H. Kuhn, Nature **134**, 25 (1934); Proc. Roy. Soc. **A148**, 335 (1935).

[2] Millman, Fox and Rabi, Phys. Rev. **46**, 320 (1934). These authors were able to determine the spin as well as the h.f.s. splitting.

[3] S. Goudsmit, Phys. Rev. **43**, 636 (1933).

[4] E. Fermi and E. Segré, Zeits. f. Physik **82**, 729 (1933).

[5] E. Fermi and E. Segré, Memorie, R. Accademia d'Italia **4**, 131 (1933).

## Wave Functions

Starting with the field of $K^+$, which has been published by Hartree,[6] we have performed a numerical integration to obtain the $4s$ wave function.[7] The results are given in Table I.

For simplification of the calculations, it is desirable to make the wave functions mutually orthogonal. The orthogonalization integrals are: $(1s, 2s)=0.0113$; $(1s, 3s)=0.00365$; $(1s, 4s)=0.000562$; $(2s, 3s)=0.0212$; $(2s, 4s)=0.00422$; and $(3s, 4s)=0.0506$. Let us denote by $P^0$ the functions after orthogonalization and normalization ($\int(P^0)^2dr=1$). Then $P^0(2s)=P(2s)-0.0113\ P(1s)$; $P^0(3s)=P(3s)-0.0212\ P(2s)-0.00341\ P(1s)$; and $P^0(4s)=1.0013[P(4s)-0.0505\,P(3s)-0.00315\,P(2s)-0.000342\,P(1s)]$. The values of the nonorthogonal wave functions $\chi=(P/r)$ at the origin are: $\chi_{1s}(0)=161.9$; $\chi_{2s}(0)=45.17$; $\chi_{3s}(0)=15.76$; and $\chi_{4s}(0)=3.124$. Before orthogonalization, $[\chi_{4s}(0)]^2=9.76$; afterwards, $[\chi_{4s}{}^0(0)]^2=4.548$. (That is, the value of the nuclear magnetic moment would be smaller by a factor of about two if the calculations were made with the nonorthogonal wave functions.)

Table I. *Normalized $P(4s)$ for potassium.*

| $r$ | $P$ | $\xi$ | $r$ | $P$ | $r$ | $P$ | $\eta$ |
|---|---|---|---|---|---|---|---|
| | | | $\epsilon=0.265$ | | | | |
| 0.000 | 0.0000 | 19.000 | 0.40 | −0.0598 | 6.0 | −0.4220 | 0.1199 |
| .005 | .0142 | 19.374 | .45 | − .0312 | 6.5 | − .3937 | .1573 |
| .010 | .0257 | 19.788 | .50 | − .0003 | 7.0 | − .3609 | .1881 |
| .015 | .0349 | 20.254 | .55 | + .0307 | 7.5 | − .3264 | .2139 |
| .020 | .0421 | 20.779 | .60 | + .0601 | 8.0 | − .2916 | .2358 |
| | | | | | 8.5 | − .2578 | .2547 |
| .03 | .0509 | 22.048 | .7 | .1105 | 9.0 | − .2261 | .2712 |
| .04 | .0540 | 23.724 | .8 | .1465 | 9.5 | − .1967 | .2857 |
| .05 | .0527 | 26.001 | .9 | .1679 | 10.0 | − .1700 | .2988 |
| .06 | .0480 | | 1.0 | .1761 | | | |
| .07 | .0409 | | 1.1 | .1734 | 11 | − .1246 | .3206 |
| .08 | .0321 | | 1.2 | .1623 | 12 | − .0896 | .3383 |
| .09 | .0220 | | | | 13 | − .0634 | .3531 |
| .10 | .0113 | | 1.4 | .1226 | 14 | − .0443 | .3656 |
| | | | 1.6 | .0699 | 15 | − .0305 | .3763 |
| .12 | −.0108 | | 1.8 | .0119 | 16 | − .0209 | .3856 |
| .14 | −.0321 | | 2.0 | − .0470 | 17 | − .0138 | .3937 |
| .16 | −.0511 | | 2.2 | − .1040 | 18 | − .0095 | .4008 |
| .18 | −.0673 | | 2.4 | − .1578 | 19 | − .0063 | .4071 |
| .20 | −.0801 | | 2.6 | − .2074 | 20 | − .0042 | .4128 |
| .22 | −.0896 | | 2.8 | − .2524 | 21 | − .0028 | .4179 |
| .24 | −.0958 | | 3.0 | − .2926 | 22 | − .0018 | .4225 |
| .26 | −.0989 | | 3.2 | − .3279 | 23 | − .0012 | .4267 |
| .28 | −.0993 | | 3.4 | − .3583 | 24 | − .0008 | .4305 |
| .30 | −.0972 | | 3.6 | − .3840 | 25 | − .0005 | .4340 |
| | | | 3.8 | − .4052 | 26 | − .0003 | .4372 |
| .35 | −.0830 | | 4.0 | − .4221 | 27 | − .0002 | .4402 |
| | | | | | 28 | − .0001 | .4429 |
| | | | 4.5 | − .4476 | 29 | − .0001 | .4455 |
| | | | 5.0 | − .4530 | 30 | − .0000 | .4480 |
| | | | 5.5 | − .4430 | 31 | − .0000 | .4502 |

## Nuclear Moment

The h.f.s. splitting of an $s$-state is given[8] by $\Delta(s)=(8\pi/3)[(2I+1)/I]\mu\mu_0\psi^2(0)$, where $I$ is the nuclear spin, $\mu_0$ is the Bohr magneton, $\mu$ is the nuclear magnetic moment, and $\psi(0)$ is the value of the wave function (normalized so that $\int\psi^2d\tau=1$) at the nucleus. We have[9] $\psi(0)=(1/4\pi)^{\frac{1}{2}}\chi(0)$, so that $\Delta(s)=(2/3)[(2I+1)/I]\mu\times\mu_0\chi^2(0)$. For $K^{39}$, $I=3/2$. Substituting numerical values, we have, if $g=(\mu/\mu_0)\times1838$,

$$0.015=\frac{(2/3)(8/3)(g/1838)(9.17\times10^{-21})^2 4.548}{(0.528\times10^{-8})^3\times19.662\times10^{-17}}.$$

Solving, $g=949\Delta(s)[I/(2I+1)][1/\chi^2(0)]=1.17$. That is, we obtain a nuclear magnetic moment about three times as large as that found by Fermi. This disagreement has its origin, of course, in the fact that different eigenfunctions have been employed. We use a Hartree function; Fermi and Segré use a one-electron function based on the statistical method, which function contains parameters to be determined from the experimental term values.

Since the article of Fermi and Segré[8] is somewhat inaccessible, we shall indicate their procedure.[10] Let the Schrödinger radial function be $\rho\psi$, where $\rho$ is the normalization factor. Then $u=r\psi$ satisfies the differential equation $(d^2u/dr^2)+(8\pi^2m/h^2)(E-eV)u=0$. The potential $V$ is found by the statistical method, and the equation solved[11] for $E=0$ by the method of Wentzel-Brillouin. One sets $u=kR\sin\theta$, where $R^2(d\theta/dr=1$. $k$ may be determined by matching such a solution with the power series development about the origin.

To evaluate $\rho$, it is supposed that at a point $\xi$ a perturbation $\lambda\delta(r-\xi)$ is introduced, where $\lambda$ is an arbitrary parameter and $\delta$ is the Dirac improper function. The first-order perturbation energy is then $\Delta E=4\pi\lambda\rho^2u^2(\xi)$. At the point $\xi$, the value of $u$ will not be changed, but there will

[6] D. R. Hartree, Proc. Roy. Soc. **A143**, 506 (1934).

[7] As usual, it has been assumed that it is unnecessary to make the field self-consistent.

[8] E. Fermi, Zeits. f. Physik **60**, 322 (1930).

[9] The value of the nuclear moment reported by us at the Pittsburgh meeting of the Am. Phys. Soc. was too small by this factor $4\pi$, which had been omitted.

[10] Certain details have been omitted by Fermi and Segré. These we have tried to reconstruct as accurately as possible.

[11] In the article by F. & S., the term "$\infty s$ eigenfunctions" is used. We interpret this to mean $s$ eigenfunctions with $E=0$. Such eigenfunctions, which were used earlier by Fermi in his calculations of the Rydberg corrections, do not differ much from the optical ones in the interior of the atom.

be a phase change $\Delta\theta$. If this were $\pi$, the number of nodes would be different by unity. Therefore, put $\Delta E=-(\Delta\theta/\pi)(dE/dn)$. The discontinuity at $\xi$ introduced by the perturbation into the first derivative of the wave function is $\Delta u'=(8\pi^2m/h^2)\lambda u(\xi)$. Now $u'=kR'\sin\theta+kR\cos\theta\times(d\theta/dr)$. Therefore

$$\begin{aligned}\Delta u' &= kR\sin\theta\Delta(R'/R)+(k/R\sin\theta)\Delta(\sin\theta\cos\theta)\\ &= kR\sin\theta\Delta(R'/R)+(k/2R\sin\theta)\Delta(\sin 2\theta)\\ &= kRR'\sin\theta\Delta(1/R)+(k/R\sin\theta)\cos 2\theta\Delta\theta\end{aligned}$$

provided that $R'$ is not appreciably altered.[12] Since $\Delta u=0$, we have $(R+\Delta R)\sin(\theta+\Delta\theta)=R\sin\theta$, or $\Delta R=-R\cot\theta\Delta\theta$. Accordingly, $\Delta(1/R)=(1/R)\cot\theta\Delta\theta$, and $\Delta u'=kR'\cos\theta\Delta\theta+(k/R\sin\theta)\cos 2\theta\Delta\theta$. Now let us choose[13] the point $\xi$ so that $\theta=\pi/2$. Then[14] $(\Delta\theta)_{\pi/2}=-(8\pi^2m/h^2)\lambda R^2$. Substituting in the expression for $\Delta E$, we finally obtain $\rho^2=(2m/h^2k^2)(dE/dn)$. The value of $k$ was determined for 15 atoms by Amaldi and Fermi,[15] and correction factors with respect to the formula $\psi^2(0)=(1/\pi a^3)(Z/2Rh)\times(dE/dn)$ were calculated for various values of $Z$. For small $Z$, the factor is approximately unity. If, then, we have a Rydberg series, we can readily compute $\psi^2(0)$ from the empirical value of $dE/dn$, so that this formula is quite useful.

The calculations of Fermi and Segré seem to us somewhat incomplete, however, since they have not found a set of mutually orthogonal single-electron wave functions. This is, apparently, the principal reason for the disagreement between our results and theirs, as may be seen by a comparison of the nonorthogonal $4s$ functions calculated by the two methods. The statistical method gives $\chi_{4s}^2(0)=13.7$; while the Hartree method results in $\chi_{4s}^2(0)=9.76$. The agreement is, in our opinion, as good as is to be expected.

We do not at present feel able to estimate how accurate the results from the Hartree method are. Experience to date seems to indicate that the Hartree functions are fairly reliable, especially when applied to scattering problems. We conclude that the value of the magnetic moment found from the Hartree method is probably the most accurate so far, but may be subject to modification when better wave functions are known. Because of this uncertainty, we have not calculated a value of the magnetic moment from the splitting of the $^2P_{3/2}$ state, for even if agreement with the value from the $^2S_{1/2}$ state were obtained, it might not be overly significant.[16]

Finally, our value of 1.2 nuclear magnetons is not as abnormally low as that found by Millman, Fox and Rabi, so that we do not consider that there is any basis for regarding the structure of the $K^{39}$ nucleus as exceptional.

[12] This will probably be the case, since $R$ is the amplitude of the oscillating function.

[13] This brings up the question as to whether the procedure is actually independent of the choice of $\xi$. Fermi and Segré do not discuss the point.

[14] This is in agreement with formula (30), p. 152, reference 5, for $\theta=\pi/2$, but we are unable to check the general validity of this formula.

[15] Reference 30 (reference 5). Apparently, this work is still unpublished.

[16] The $^2P$ state is probably perturbed, according to Fermi and Segré (reference 5, p. 141).

# The Dielectric Constants of Air and Hydrogen at High Pressures

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The dielectric constants of air and hydrogen at pressures from 71.8 to 334.7 atmospheres at 20°C have been measured. The values were obtained by measuring, with a capacity meter of the heterodyne type, the variation with pressure of the capacity of a fixed condenser fitted into the pressure vessel. The frequency was 2500 kilocycles. The dielectric constants obtained are slightly lower than those of Tangl and Broxon for pressures about 80 atmospheres. The Clausius-Mosotti function $(\epsilon-1)/d(\epsilon+2)$ was calculated for each pressure. The change with pressure for air is small and irregular, average 1.43. For hydrogen the value decreased uniformly from 1.16 at 71.8 atmospheres to 0.99 at 334.7 atmospheres.

## INTRODUCTION

THE development of a differential manometer for use with hydrogen and air over the pressure range 1 to 340 atmospheres in which the deflection of a diaphragm changed the capacity between attached condenser plates, required that the dielectric constant of the gases be known. Measurements of the dielectric constant of air have been made to the pressure of 170 atmospheres; while for hydrogen, some work has been done on pressures to 194 atmospheres. The dielectric constant of air at pressures up to 170 atmospheres has been determined at low frequencies or by static methods by Tangl,[1, 2] Waibel[3] and Broxon.[4] Jordan, Broxon and Walz[5] have made measurements of the dielectric constant of air at pressures up to 170 atmospheres and at frequencies of 1 to 70 kilocycles. Occhialini,[6] using a frequency of about 10,000 cycles, obtained results which were lower than those of the other workers mentioned here.

## DESCRIPTION OF APPARATUS

A fixed air condenser was made to fit into a pressure vessel and variation of capacity of this condenser with pressure was measured with a capacity meter of the heterodyne type, operating at a frequency of 2500 kilocycles.

The gas, from a Rix compressor, was cooled to about 15°C and passed through a baffle-plate type separator and then through a filter consisting of six inches of tightly packed felt. This arrangement removed all of the oil and lowered the water concentration to 0.015 percent. Moisture determinations were made by drying samples over Desic-chora. After the filter, the gas flowed through a coil of 1.5-millimeter diameter copper tubing where it was brought to room temperature, which was kept constant (±1°C) throughout the entire series of measurements. A cylindrical steel pressure vessel, having inside dimensions of 9 cm diameter by 6 cm, was connected through appropriate valves to the tubing. A Bourdon type gauge which, for this work, had been calibrated on a dead weight tester was in the line. The accuracy of the pressure measurements was at least one percent.

The condenser shown in Fig. 1 was fastened to the bottom of the pressure vessel and the electrical lead to it carried through an isolantite bushing in the top of the steel shell. A spring attached to the bushing made contact with the top plate of the condenser.

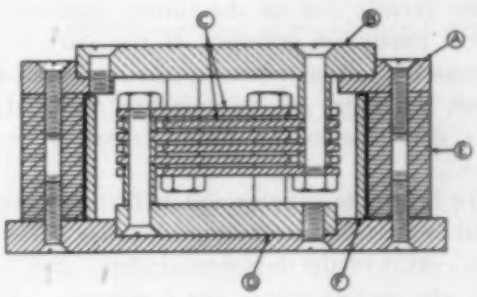


FIG. 1. Condenser construction.

[1] Karl Tangl, Ann. d. Physik **23**, 559 (1907).
[2] Karl Tangl, Ann. d. Physik **26**, 59 (1908).
[3] F. Waibel, Ann. d. Physik **72**, 161 (1923).
[4] James W. Broxon, Phys. Rev. **37**, 1338 (1931).
[5] A. R. Jordan, J. W. Broxon and F. C. Walz, Phys. Rev. **46**, 66 (1934).
[6] A. Occhialini, Physik. Zeits. **6**, 669 (1905).

In order to make correction for the effect of solid insulation, the condenser was built so that the parallel condenser plates, upon which the change in capacity with pressure was determined, were isolated from the solid insulation by means of shielding and could be removed from the frame of the condenser and replaced without change in capacity. This was accomplished by mounting the condenser plates $C$ on end plates $B$ and $D$ which were in turn fastened to the frame of the condenser in such a way that the entire assembly of condenser and end plates could be removed from the frame as a unit. The top ring of the frame was insulated from the bottom plate by four isolantite posts $E$ which were shielded from the condenser plates by the cylinder $F$ fastened to the bottom plate and separated from the top plate by a 0.3-millimeter gap.

**Capacity meter**

The high frequency heterodyne type capacity meter, shown in Fig. 2, was used in which the unknown capacity acted as the tuning condenser of the "manometer oscillator" which employed a modified Hartley circuit. The plate end of the oscillatory circuit was grounded and current was carried to the tube filament through the double-wound coil $L_4$–$L_5$. This circuit required the use of only one bushing through the shell of the pressure vessel and allowed the base of the condenser and the shielding to be fastened directly to the grounded shell.

Another oscillator, which also acted as a detector, was coupled to the manometer oscillator by means of a low impedance link circuit. This consisted of single loops coupled to the oscillator coils connected by a twisted pair, one conductor of which was grounded. The standard Hartley circuit was used in this detector unit. An accurate vernier dial on the tuning condenser $C_1$ gave a maximum accuracy of one part in one thousand. $C_2$ is a trimming condenser used to adjust the range of the capacity meter. Both units were shielded by means of heavy copper boxes.

The beat note between the oscillators could be heard in the telephone receivers connected in the plate circuit of the detector-oscillator unit. Zero beat, the setting where the frequencies of the two oscillators were exactly equal, was the point

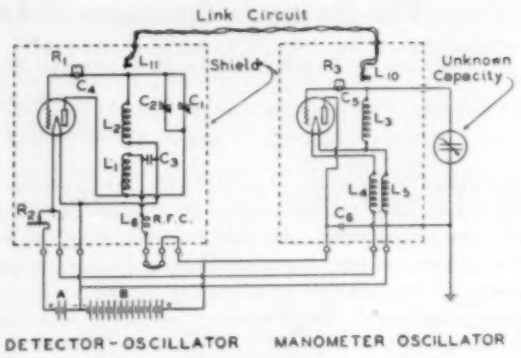


FIG. 2. Circuit for the high frequency heterodyne capacity meter.

at which readings were made. The use of a moderately high frequency, two to three megacycles, the stability of the oscillators and the very loose coupling between them minimized the effect of "pulling in" to such an extent that the zero beat method could be used without difficulty. Since both the oscillators were connected to the same power supply the factors which would cause the frequency of an oscillator to drift would cause both to drift the same direction by the same amount. This would not affect the frequency differences and consequently changes in plate and filament potential and variation in temperature had little effect on the calibration. This apparatus was built rigidly enough so that there could not be any change of its calibration because of mechanical distortion of its component parts.

## EXPERIMENTAL PROCEDURE

The capacity meter was calibrated against a General Radio Type 222 precision condenser. This condenser was substituted for the unknown capacity and readings made at frequent intervals on the scale. Calibrations were made after each set of dielectric measurements and the maximum difference between corresponding points on the various calibrations was found to be less than 0.2 percent. As a further check on the calibration, a second variable condenser was placed across the standard condenser and the lower end of the standard condenser scale checked against other sections by means of the capacity meter.

Air or hydrogen at 340 atmospheres was

slowly released into the pressure vessel which contained the fixed condenser. At intervals of about 70 atmospheres, the inflow of gas was stopped and the capacity of the condenser was measured. The system was allowed to stand at each pressure until the capacity remained constant, although the change that did occur at first was negligible. After the maximum pressure had been reached, the measurements were repeated with decreasing pressure.

The pressure vessel was then opened and the plate assembly removed from the condenser. A blank cover plate of exactly the same dimensions as the top plate $B$ Fig. 1, was put on the frame and the pressure vessel again closed. The gas was run in and capacity measurements made for each pressure in the manner previously described. These measurements gave the variation with pressure of the capacity of the condenser frame, solid insulation, contact spring, and shielding.

When the condenser is assembled with the plates in, it may be considered to consist of the capacity between the plates, the dielectric of which is entirely air, in parallel with the capacity of the shielding, frame, insulation, etc., some of which are solid dielectrics. The dimensions of the exterior of the condenser were exactly the same whether the blank cover plate or the plate $B$ were in, so that the capacity between the condenser and pressure vessel was the same in both cases. Therefore, the difference between the capacities with the plates $C$ in and with them out represented the capacity of these plates with each other and with the surrounding shielding. No solid insulation was in the field of this capacity. Consequently the variation, with change in pressure, of this difference $C_0-c_0$ where,

$C_0$ = capacity at 1 atmosphere with plate $C$ in,
$c_0$ = capacity at 1 atmosphere with plate $C$ out,

was a capacity on which the solid dielectric of the condenser had no effect.

One of the difficulties encountered in this circuit was the change in reactance of some of its components with the change in capacity of the condenser inside the pressure vessel. The worst offender in this respect was the bushing through the pressure vessel shell. The value of $C_0-c_0$ was measured with the condenser outside of the pressure vessel and found to be 2.0 mmf less

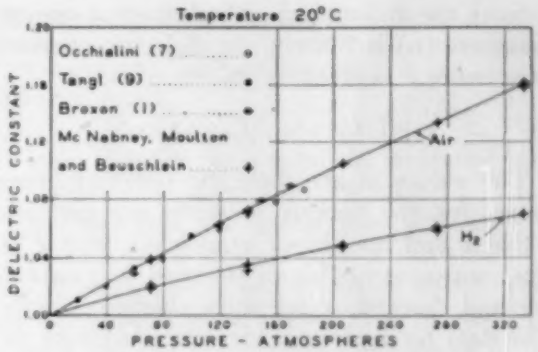


FIG. 3. Dielectric constant of air and hydrogen as a function of pressure.

than the value of $C_0-c_0$ for the condenser when in the pressure vessel. A variable condenser was placed across the terminals of the capacity meter, the ungrounded lead of which ran through the bushing. The apparent capacity of the bushing was then measured for various settings of the condenser. Between the capacity settings corresponding to $c_0$ and $C_0$, respectively, the capacity of the bushing was found to increase 2.0 mmf. This accounts for the discrepancy in the values of $C_0-c_0$. Correction was made for this variation in the results. The error introduced by the difference in resistance between the standard and substituted condenser when the bushing was not in the circuit was in the order of 0.005 percent, which could be neglected. The mechanical strength required of a bushing to withstand such high pressures requires a type of construction in which the electrical losses are high and the reactance variable.

In the dielectric constant determination of air the accuracy of $(\epsilon-1)$ was about one percent of the maximum value while for hydrogen the accuracy on this basis was about two percent.

TABLE I. *Dielectric constants of air and hydrogen.* Frequency 2.5 megacycles. Temperature 20°C.

| Press. (Atmos.) | Air — Dielectric constant ($\epsilon$) Run 1 | Run 2 | $\left(\frac{\epsilon-1}{\epsilon+2}\right)\times\left(\frac{1}{d}\right)10^{6}$ * | Hydrogen — Dielectric constant ($\epsilon$) Run 1 | Run 2 | $\left(\frac{\epsilon-1}{\epsilon+2}\right)\times\left(\frac{1}{d}\right)10^{6}$ |
|---|---|---|---|---|---|---|
| 72.0 | 1.039 | 1.039 | 1.47 | 1.019 | 1.021 | 1.16 |
| 140.0 | 1.073 | 1.071 | 1.40 | 1.032 | 1.036 | 1.07 |
| 208.0 | 1.106 | 1.105 | 1.41 | 1.048 | 1.050 | 1.05 |
| 274.0 | 1.134 | 1.134 | 1.42 | 1.059 | 1.061 | 1.00 |
| 335.0 | 1.162 | 1.159 | 1.45 | 1.070 | 1.070 | 0.99 |

* Values of $d$ were calculated from I.C.T.

Since the dielectric constant of air at one atmosphere ($\epsilon_1$) is 1.00059, the dielectric constant at pressure $P$ is given by the equation,

$$\epsilon_P=[(C_P-c_P)/(C_0-c_0)](\epsilon_1).$$

The values of the dielectric constant determined for the various pressures are given in Table I and are shown graphically in Fig. 3. The measurements for air obtained with ascending and descending pressures checked exactly. The data for hydrogen were obtained with descending pressures only. This showed that there was no hysteresis effect. Data on the compressibility of isolantite were not found in the literature. An estimate of the error due to the compressibility was made by using data given for soapstone, a similar material. The displacement of the plates at 350 atmospheres pressure was estimated to be 0.3 percent of the plate spacing, causing a change in capacity of less than 0.05 percent. The values so obtained are slightly lower than those of Tangl and of Broxon for pressures above 80 atmospheres, and the slopes of the curves decrease slightly as the pressure increases for both air and hydrogen. According to the Clausius-Mosotti equation:

$$[(\epsilon-1)/(\epsilon+2)](M/d)=\text{constant};$$

$\epsilon$=dielectric constant; $M$=molecular weight; $d$=density. The Clausius-Mosotti function $[(\epsilon-1)/(\epsilon+2)]/d$, was calculated for each pressure and is shown in the tabulated results. In these results, the change in the Clausius-Mosotti function with pressure for air is small and irregular, while for hydrogen the function decreases with increase in pressure.

The curvature of the pressure-dielectric constant line for air may be due either to an effect of the high frequency at high gas densities, or to some irregularity in the operation of the capacity meter. Jordan, Broxon and Walz,[5] using the apparatus of Broxon[4] showed that the change of dielectric constant of air with frequency was very small over the pressure range 1 to 170 atmospheres and a frequency range of zero to 70 kilocycles. The experimental results for air shown in Fig. 3 fall below those of Tangl[1, 2] and of Broxon[4] and above those of Occhialini.[6] The frequency used in this work was 2.5 megacycles while Talbot[7] working at a pressure of one atmosphere found no appreciable change in the dielectric constant over the frequency range of 0.025 to 1.100 megacycles. The frequency and some of the pressures used in this experimental work are beyond the range of the above determinations.

Broxon[4] has compared the results of dielectric constant determinations found in the literature and has concluded that those made at high frequencies are not consistent among themselves while those at low frequencies are in agreement. Cagniard[8] pointed out that many of the investigators using high frequency methods had difficulty with instability of their oscillating circuits. No instability was encountered in the apparatus described in this paper; but, as has been previously mentioned, other factors may have caused apparent changes in capacity. Further research in the measurement of capacities at high frequencies is desirable because the heterodyne capacity meter, using high frequency oscillators, has characteristics which make its use advisable, and sometimes necessary for many practical applications of capacity measurements.

[7] F. L. Talbot, Thesis in Physics, Catholic University of America, Washington, D. C., 1928.
[8] L. Cagniard, Ann. de Physique **9–10**, 460 (1928).

## Errata: Ionization Area of He and Bethe's Theory

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(Phys. Rev., **43**, 839 (1933))

ACCORDING to Bethe's[1] theory of ionization by impact the area effective for ionizing a $K$ shell at any voltage $U$ times the ionization voltage $V_K$ should be

$$\Phi(U)=\frac{\pi e^2}{V_K^2}\cdot\frac{2b}{U}\ln\frac{4U}{B},$$

provided $U$ is large enough, with $b$ and $B$ pure numbers depending on the atomic number but not on $U$. In reporting data on Ag and looking for evidence on how large $U$ must be for testing this theory, we compared this equation with Smith's[2] data on He. For this purpose we plotted a graph using the $b$ and $B$ given by Bethe's Eq. (54b) for the ionization of the H atom, namely 0.285 and 0.048, respectively. In writing the paper, however, we inadvertently recorded for $b$ the value 1, which belongs to the H atom, but for the sum of the ionization and excitation areas, along with $B=0.638$.

The fact that our graph does not fit our recorded $b$ and $B$ has just come to our attention in a paper by Liska;[3] and in looking up our notes we have found an arithmetical error also. To correct this, our graph should be lowered by 14 percent. This change, however, does not change our conclusion that Bethe's equation holds well for He at high voltages but not at all in our range $U\leqq 7$. Likewise this change has no effect whatever on our data or our comparisons with theories for Ag. For He the best comparison with Bethe's theory is that of Liska, who sets $B$ at 0.048 and then treats $b$ as an empirical constant, finding a value 0.291, very near Bethe's 0.285.

[1] H. Bethe, Ann. d. Physik **5**, 325 (1930).
[2] P. T. Smith, Phys. Rev. **36**, 1293 (1933).
[3] J. W. Liska, Phys. Rev. **46**, 169 (1934).

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## Proceedings of the Metropolitan Section of the American Physical Society

### MEETING OF MARCH 22, 1935

THE second meeting of the Metropolitan Section of the American Physical Society for the season 1934–1935 was held on Friday, March 22, 1935, in Room 301 of the Physical Laboratory of Columbia University in New York City. An afternoon and an evening session were held. The presiding officer was Professor H. C. Urey.

The following papers were presented:

*Afternoon Session*

**Prediction of Atomic Energy States,** R. F. BACHER
**Measurement of Nuclear Magnetic Moments from Hyperfine Structure Data,** L. P. GRANATH
**Nuclear Moments from Molecular Beams,** I. I. RABI
**Isotope Effect in Polyatomic Molecules,** W. S. BENEDICT

*Evening Session*

**Methods of Separation of Isotopes,** H. C. UREY

In the afternoon session the following officers were elected for the season 1935–1936:

| | |
|---|---|
| Chairman | H. C. Urey |
| Vice Chairman | A. C. G. Mitchell |
| Secretary-Treasurer | W. S. Gorton |
| Elected members of the Executive Committee | H. D. Smyth<br>M. W. Zemansky |

W. S. GORTON, *Secretary-Treasurer*

# LETTERS TO THE EDITOR

*Prompt publication of brief reports of important discoveries in physics may be secured by addressing them to this department. Closing dates for this department are, for the first issue of the month, the twentieth of the preceding month; for the second issue, the fifth of the month. The Board of Editors does not hold itself responsible for the opinions expressed by the correspondents.*

## The Hylleraas Method Applied to Lithium

It has been shown by the work of Hylleraas[1] on He and of the authors[2] on $H_2$ that two-electron problems can be satisfactorily solved by the variation method with wave functions which provide for the expression of polarization effects (the instantaneous distortion which each electron produces upon the orbit of the other). A series of terms is prepared, starting with a leading term of approximately the form which would be a solution of the problem if the effects of electronic repulsions could really be replaced by those of static screening charges. Other terms are derived from this by multiplying it with simple combinations of powers of the coordinates of the individual electrons, and of their mutual separation. The final wave function is a linear combination of these terms, with coefficients determined by the variation process.

We have extended this method to a three-electron problem, the ground state of Li. Unfortunately, the pressure of other work will force us to delay the presentation of a full analysis and report upon the problem; we wish here to communicate the bare results obtained. We give below the total energy as computed in atomic units ($e^2/a_0 = 27.08$ volts). Using a wave function constructed from the same series, after removing one electron, we have also computed the energy of the ion; we give here the difference between these two quantities, as the ionization energy. For comparison, we include the results of Wilson[3] (the best previous calculation), and the observed values.[4]

*Energy of Lithium Atom*

| | Total | Ionization | |
|---|---|---|---|
| | $e^2/a_0$ | $e^2/a_0$ | volts |
| Experimental | 7.4783 | 0.1981 | 5.364 |
| Wilson | 7.4192 | 0.1965 | 5.320 |
| James and Coolidge | 7.4757 | 0.1975 | 5.347 |

These results were obtained with a series of 15 terms, of which 5 involved distances between electrons of the $K$-shell and that of the $L$-shell. Although the mutual polarization of the $K$ electrons is undoubtedly greater, we contented ourselves with two terms, taking account of this, because our chief interest lay in the ionization energy, and it soon became clear that this would not be affected if the wave function contained small errors referring exclusively to the inner-shell electrons. Such errors raise the energies of the atom and of the ion by practically the same amounts. There is no reason to doubt that it would be easy to get a considerable improvement in the result for the total energy by putting in two or three additional simple terms involving mutual polarization of the $K$ electrons. The residual error in the ionization energy seems much more obstinate. A survey of the probable improvement obtainable from certain untried terms whose effect can be predicted with some assurance does not promise more than 0.007 volt. The success of the method is therefore comparable to the case of the first excited level of parhelium,[5] where also there is involved the reaction between $1s$ and $2s$ electrons of the same spin.

HUBERT M. JAMES
ALBERT SPRAGUE COOLIDGE
Research Laboratory of Physics,
Mallinckrodt Chemical Laboratory,
Harvard University,
April 4, 1935.

[1] E. A. Hylleraas, Zeits. f. Physik **54**, 347 (1929).
[2] H. M. James and A. S. Coolidge, J. Chem. Phys. **1**, 825 (1933).
[3] E. B. Wilson, Jr., J. Chem. Phys. **1**, 210 (1933).
[4] A. Ericson and B. Edlén, Zeits. f. Physik **59**, 656 (1930).
[5] E. A. Hylleraas and B. Undheim, Zeits. f. Physik **65**, 759 (1930).

## Analysis of Data on Radioactivity Induced by Neutron Bombardment

Though 47 elements are reported to be activated by neutron bombardment the literature gives the isotope involved and the type of transmutation for only 27. These 27 are classified in Table I. Group I of this table contains those activated by simple capture of a neutron; group II, those activated by capture of a neutron with emission of a proton; and group III, those activated by capture of a neutron with alpha-emission. $Z$ (the atomic number), $M$ (the mass number), and $M-Z$ are also recorded for each parent isotope. The following facts are apparent:

TABLE I. *Elements activated to radioactivity by neutron bombardment* Classified according to type of transmutation.

| I. Simple Capture | | | | II. Proton Emission | | | | III. Alpha-Emission | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | $Z$ | $M$ | $M-Z$ | | $Z$ | $M$ | $M-Z$ | | $Z$ | $M$ | $M-Z$ |
| Na | 11 | 23 | 12 | Mg | 12 | 24 | 12 | F | 9 | 19 | 10 |
| K | 19 | 41 | 22 | Al | 13 | 27 | 14 | Al | 13 | 27 | 14 |
| V | 23 | 51 | 28 | Si | 14 | 28 | 14 | P | 15 | 31 | 16 |
| Mn | 25 | 55 | 30 | P | 15 | 31 | 16 | Cl | 17 | 35 | 18 |
| Cu | 29 | 63 | 34 | S | 16 | 32 | 16 | Sc | 21 | 45 | 24 |
| Cu | 29 | 65 | 36 | Ca(?) | 20 | 40 | 20 | Mn | 25 | 55 | 30 |
| As(?) | 33 | 75 | 42 | Cr | 24 | 52 | 28 | Co | 27 | 59 | 32 |
| Br | 35 | 79 | 44 | Fe | 26 | 56 | 30 | All $Z$'s and $M$'s odd. | | | |
| Br | 35 | 81 | 46 | Zn | 30 | 64 | 34 | In every one of the 27 cases, $M-Z$ is even. | | | |
| I | 53 | 127 | 74 | Zn | 30 | 66 | 36 | | | | |
| All $Z$'s and $M$'s *odd*. | | | | 8 of the 10 $Z$'s and $M$'s even. | | | | | | | |

(?) The two cases indicated with this mark in this table, Table II and Fig. 1 are somewhat doubtful.

(1) *M–Z is even for all known parent isotopes.*

(2) *M and Z are odd numbers for all parent isotopes activated by simple neutron capture or by capture with alpha-emission.*

(3) *M and Z are even numbers for 8 of the 10 cases with proton emission*, the two exceptions being Al and P.

Table II shows all the known active products produced

TABLE II. *List of identified active products and final isotopes.*

| (1) Radio-Element | (2) Atomic Number (*Z*) | (3) Mass Number (*M*) | (4) *M–Z* | (5) Final Stable Isotope | (6) Relative Abundance (%) |
|---|---|---|---|---|---|
| N | 7 | 16 | 9 | * O 16 | 99.76 |
| Na | 11 | 24 | 13 | * Mg 24 | 77.4 |
| Mg | 12 | 27 | 15 | * Al 27 | 100 |
| Al | 13 | 28 | 15 | * Si 28 | 89.6 |
| Si | 14 | 31 | 17 | P 31 | 100 |
| P | 15 | 32 | 17 | S 32 | 96 |
| K(?) | 19 | 40 | 21 | * Ca 40 | 97 |
| K | 19 | 42 | 23 | Ca 42 | 0.8 (3rd) |
| V | 23 | 52 | 29 | Cr 52 | 81.6 |
| Mn | 25 | 56 | 31 | * Fe 56 | 95 |
| Cu | 29 | 64 | 35 | Zn 64 | 50.4 |
| Cu | 29 | 66 | 37 | Zn 66 | 27.2 (2nd) |
| As(?) | 33 | 76 | 43 | Se 76 | 9.5 (3rd) |
| Br | 35 | 80 | 45 | Kr 80 | 2.45 (5th) |
| Br | 35 | 82 | 47 | Kr 82 | 11.79 (3rd) |
| I | 53 | 128 | 75 | X 128 | 2.30 (7th) |

* These six elements compose over 93% of the earth's crust.
(?) Doubtful.

with their values of *Z*, *M* and *M–Z*. We see that:

(4) *M–Z is odd in every instance* (a necessary condition since *M–Z* is even for each of the parent isotopes).

(5) *M is even and Z odd for every active product except Mg 27 and Si 31*, the transmutation products of the Al and P mentioned in (3).

Assuming that all these active products are beta-rayers (as stated in the literature) it is true without exception for both the heavy radioactive elements and for those produced up to the present by neutron bombardment, that even isotopes of odd elements emit beta-rays.

In the fifth column of Table II are listed the isotopes resulting from the beta-disintegrations. Comparison with a table of known stable isotopes[1] reveals that

(6) *Every one of these 16 isotopes is a known stable isotope.* The sixth column of Table II records the relative abundance in nature of each of these isotopes, expressed as a percentage and also in order of abundance, where necessary. This column shows that

(7) *In all known cases of Z less than 30 the final stable product is the most abundant isotope* (neglecting of course the isotopes of lesser abundance when more than one occurs for a given element, as is the case for Ca and Zn);

(8) *The list of final stable products includes six elements which constitute over 93 percent of the earth's crust.*[2] These six are: O, Mg, Al, Si, Ca and Fe.

(9) *Five of these six abundant elements*, namely, Mg, Al, Si, Ca and Fe, *are activated by capturing a neutron with emission of a proton;* and the most abundant of all, oxygen, has not been found to be activated. The fact that these five isotopes return to their original form may be a partial explanation of their great abundance.

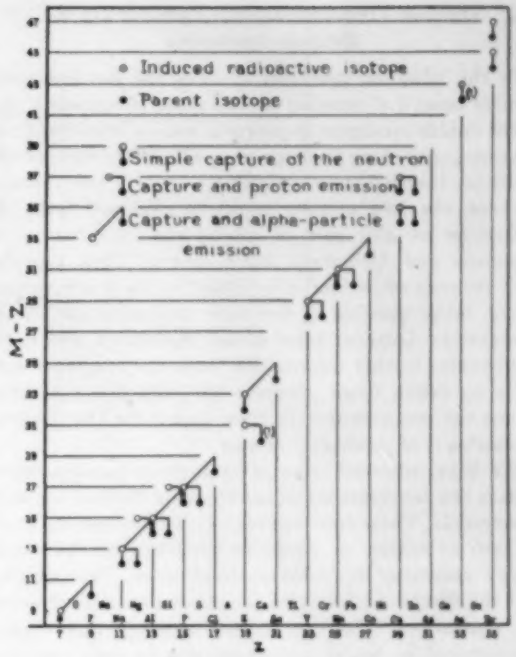


FIG. 1.

(10) Another fact which emerges is that *in every case except K 41 the isotope activated is the most abundant one.* However, this may not be significant, because of the greater difficulty of detecting the activation of isotopes present in minute proportions.

Fig. 1 is a plot of *M–Z versus Z*, to represent the neutron transmutations of elements of atomic number less than 36. Five others above atomic number 36 are not shown in this figure. Solid circles represent the parent substances; open circles represent the radioactive substances produced. A single vertical line represents a simple capture; a right-angle path represents capture with proton emission; a 45-degree path represents capture with alpha-emission. Though there is considerable evidence of order in the transformations thus far analyzed, the results are as yet too fragmentary to permit of complete generalization.

In addition to the isotopes listed in Table I there are two others, Ir and Au, which are known to become radioactive by simple capture. These are not included in the list because the isotopes responsible are not given in the literature. However, since their atomic numbers are odd, it is to be expected that they have only odd isotopes. If so, the rules given for the elements in group I of Table I apply also to these two transmutations.

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University of North Carolina,

ARTHUR E. RUARK

University of North Carolina,
April 3, 1935.

[1] Bleakney, Mueller and Barton, Rev. Sci. Inst. **6**, 59 (1935).
[2] Rutherford, Chadwick and Ellis, *Radiations from Radioactive Substances*, p. 526.

### The Low Frequency Double Vibrations of the Deutero-Ammonias

In the vibration spectrum of $NH_3$ the low frequency parallel band ($\nu_3$) consists of two close components, due to the double minimum in potential energy with respect to the coordinate along the symmetry axis. If the form of this potential function were completely known, the distance between the two minima could be obtained from the separation of any pair of vibrational components, as Dennison and Uhlenbeck have shown.[1] This, together with the moment of inertia indicated by the fine structure, would make possible a complete determination of the interatomic distances from measurements on one band. Conversely, further information from the spectrum may serve to define more precisely the potential constants. Hence the measurement of these bands for the deutero-ammonias is of particular interest.

We have observed pairs of absorption maxima representing the zero branches of $\nu_3$ for each of the four varieties of ammonia. These converge rapidly with increasing mass, but not as rapidly as would be predicted by the simple theory assuming infinitesimal amplitudes. This suggests that the effects of interaction are important in determining the separations. The two hybrid molecules are slightly assymetrical, of course, and would require some modification of the theoretical treatment. The positions of the observed absorption maxima in $cm^{-1}$ and their separations are as follows:

| | | | |
|---|---|---|---|
| $NH_3$ | 933 | 967 | 34 |
| $NH_2D$ | 874 | 894 | 20 |
| $NHD_2$ | 808 | 818 | 10 |
| $ND_3$ | 745 | 748 | 3 |

The molecular dimensions can best be determined by a comparison of the moments of inertia of $NH_3$ and $ND_3$ as obtained from an analysis of the rotational structure of their parallel type bands. These observations are now almost complete and will be published shortly.

We are indebted to Professor Taylor of Princeton University for a sample of very pure $ND_3$. An earlier mixed sample was supplied by Mr. Wells A. Webb, through a grant from the Faculty Research Fund.

E. F. Barker,
Marcel Migeotte*

University of Michigan,
April 17, 1935.

[1] Dennison and Uhlenbeck, Phys. Rev. 41, 313 (1932).
* C. R. B. Fellow.

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### Nuclear Reactions and Their Classification by Atomic and Isotopic Numbers

Since 1915 the writer has used the isotopic number ($I$) and the atomic number ($Z$) to exhibit the relations of atomic species and their transformations, and these variables have been found to give much more simple diagrams than those in which the atomic mass ($M$) and ($Z$) are used. The relations between some of the dependent variables involved have been presented by Harkins and Madorsky.[1] They give the formula of any nucleus as

$$(p_Z e)_Z \quad (pe)_I, \tag{1'}$$

in which $pe$ is taken as representing a neutron (page 137).

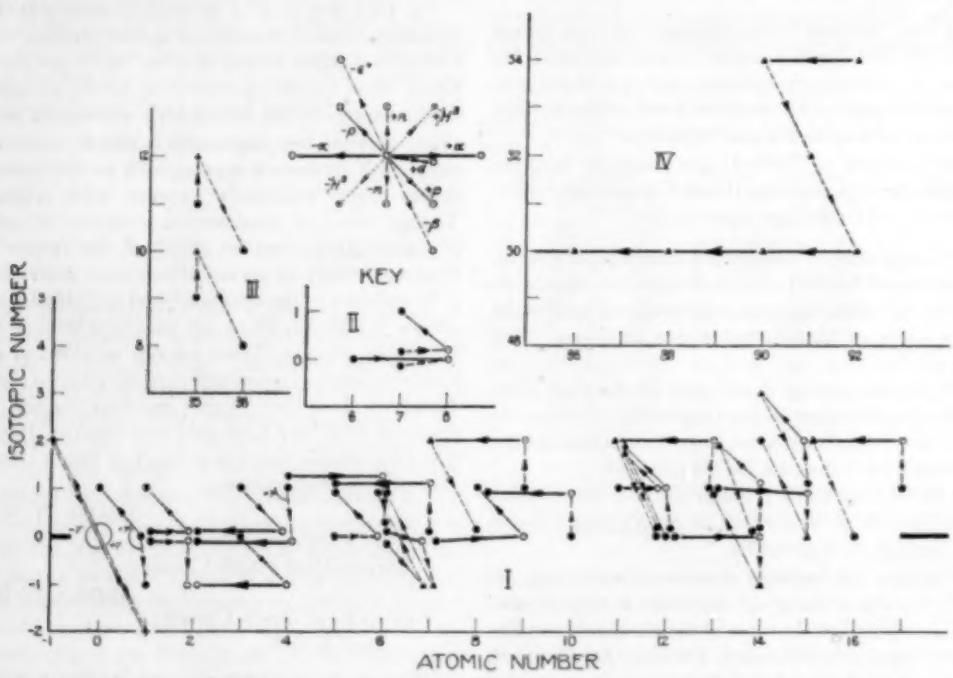


FIG. 1. Reactions of atomic nuclei. Black circles, initial or final stable nuclei; open circles, nuclei which disintegrate immediately on account of an excess of energy introduced with the projectiles and triangles, radioactive nuclei.

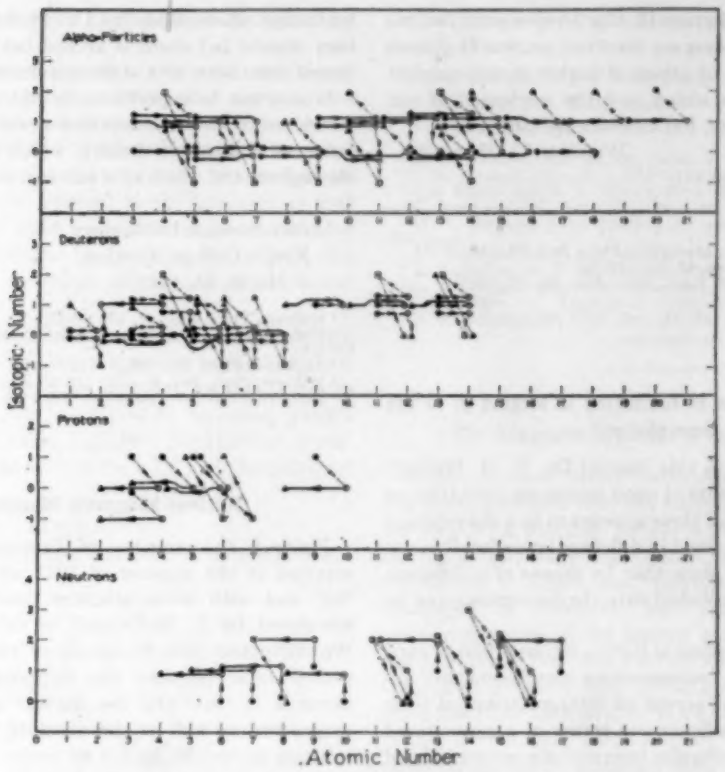


FIG. 2. Nuclear reactions arranged according to the projectiles used: neutrons, protons, deuterons and alpha-particles. The transformations due to $\gamma$-rays are given in Fig. 1. A transformation of ${}_5B^{11}$ of the type $+\alpha-p$ to ${}_6C^{14}$, which may be radioactive (total change $+\alpha-p-e$) was omitted by mistake. Certain uncertain transformations have been omitted until better evidence is obtained. An apparently partly empty section around neon is due to the fact that little work has been done with this element. Transformations of the type $+d-n-\pi$ are seen to be very similar to those of $+\alpha-n-\pi$. With neutrons either two or three steps of the transformation $+n-\alpha-e$ occur frequently. With protons the most common change is $+p-\alpha$. Here the positive sign indicates that the particle is added, the negative that it is emitted, and $p$ represents the proton, $e$ the negative electron and $\pi$ the positive electron.

Thus if $n$ represents a neutron the formula becomes

$$(pn)_Z n_I \qquad (1)$$

and this is supposed to represent any nucleus, since while $I$ is in general positive it was found to be negative for the proton. This Eq. (1) is a sufficient definition of the isotopic number. However, let

$$M-Z=N \text{ (total number of neutrons)}$$

then[2]

$$I=M-2Z=N-Z=2N-M. \qquad (2)$$

Table I shows that the variables $Z$ and $I$ give a remarkably simple representation of nuclear reactions. This table does not give all of the individual reactions, but presents practically all of the well-established types. The projectiles for which the reactions are given are the positive and negative electron ($\pi^+$, $\beta^-$) the neutron ($n$), the deuteron ($d$), the $\alpha$-particle, and a $\gamma$-ray or photon. It is seen that all transformations in this type of diagram are represented by horizontal or vertical lines, or by straight lines of slope $-1$ or $-2$ (see key).

Atomic species which are represented by open circles are in an excited state due to the energy which has been absorbed on account of the capture of the projectile, while those represented by triangles exhibit the phenomenon of radioactivity.

In the preparation of this chart use has been made of the proof by Harkins and Gans[3] that collisions in which the projectile is not captured do not in general lead to disintegration.

A chart similar to Fig. 1, but in which the reactions due to the different projectiles are arranged one above the other, but with common lines for ($Z$) shows that all of the reactions given by a single type of projectile are of relatively few simple types (see Fig. 2). A general diagram in which all of the individual reactions are plotted is not too complicated for use, especially if it is compared with the chart for the

individual projectiles. Section II, Fig. 1 represents two reactions in which deuterons are involved, section II gives a behavior characteristic of atoms of higher atomic number in which a neutron is added and the nucleus does not immediately disintegrate, but exhibits radioactivity.

WILLIAM D. HARKINS

University of Chicago,
April 12, 1935.

[1] W. D. Harkins and S. L. Madorsky, Phys. Rev. **19**, 136 (1922).
[2] W. D. Harkins, Phil. Mag. **43**, 315 (1921).
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## The Seasonal Variation of Ionization in Region $F_2$ of the Ionosphere

In his recent letter[1] in this journal Dr. E. O. Hulburt refers to the measurements of noon maximum ionization in Region $F_2$ and states that there appears to be a discrepancy between the results obtained in different latitudes. It is my object in this letter to show that by means of a different interpretation of the published data the discrepancy can be satisfactorily removed.

If we reject the contention of Kirby, Berkner and Stuart[2] that critical frequency measurements merely indicate absorption phenomena and accept an interpretation[3] of their electron-limitation significance in terms of a pronounced seasonal variation of molecular temperature, we are obliged to conclude that noon Region $F_2$ maximum ionization in temperate latitudes does not follow the expected seasonal variation and is actually slightly higher on a winter noon than on a summer noon. Dr. Hulburt correctly points out that if my interpretation on these lines is accepted there is a discrepancy between this result and other evidence. He refers in particular to the ratio (1.5 to 1.8) for summer to winter noon ionization, quoted by me in a general ionospheric discussion in London, and which was, in fact, calculated from Dr. Hulburt's own values of short wave "skipped distances." The discrepancy can therefore be narrowed down to the difference between the interpretation of critical-frequency measurements made with medium wavelengths at short distances and with short wavelengths at large distances. It means, briefly, that my interpretation of the local ionospheric measurements indicates that the maximum Region $F_2$ noon ionization is slightly less in winter than in summer, whereas Dr. Hulburt's "skipped distance" data indicate, as he himself has shown,[4] that Region $F_2$ ionization is 1.5 to 1.8 times as great on a summer noon as on a winter noon.

It would be improper for me to question the accuracy of Dr. Hulburt's measurements of "skipped distances" were it not for the fact that other measurements of similar character, made by C. R. Burrows[5] in America, yield entirely different results which are in good agreement with the local ionospheric measurements, in that the measured critical frequency is less on a summer noon than on a winter noon. It is true that Burrows interprets his results in terms of absorption-limitation, but if we regard both local and long-distance measurements as referring to electron-limitation phenomena (as Dr. Hulburt and I agree that they should be) there is accord between the conclusions drawn from both sets of measurements.

It may not be superfluous to add that this discussion is restricted to *noon* measurements and not to the maximum value of ionization density which may be experienced throughout the whole of a summer or winter day.

E. V. APPLETON

Halley-Stewart Laboratory,
King's College, London,
March 23, 1935.

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[2] Kirby, Berkner and Stuart, Bur. Standards J. Research **12**, 16 (1934).
[3] Appleton, Phys. Rev. **47**, 89 (1935).
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[5] Burrows, Proc. Inst. Rad. Eng. **19**, 1634 (1931).

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## Nuclear Magnetic Moment of $Na^{23}$

Through the courtesy of Professor Hartree we were supplied in the summer of 1933 with s.c.f. functions for $Na^+$ and with series electron functions for $3s$, $3p$, $4p$ calculated by J. McDougall in collaboration with him. We computed then by means of these functions the expected ratio between the hyperfine structure interval factor $a$ in $cm^{-1}$ and the nuclear moment $\mu$ in nuclear magnetons as well as the absolute value of the doublet splitting $\Delta\nu$ for the $3p$ and $4p$ terms.

The theoretical values of the gross doublet splittings disagree with experiment by roughly the same large factor by which the Hartree function result for the h.f.s. disagrees with the Landé-Fermi-Goudsmit formulas. These discrepancies were brought out in the symposium on nuclear moments[1] in June, 1934, and it was emphasized that in view of them one cannot be sure of the theoretical conclusions about the values of nuclear moments for any but the simplest atoms.

For $3s$, by taking into account only the energy of the series electron in the central field, the effective quantum number $n^* = 1.75$ as compared with 1.63 experimentally. Correcting for interaction with inner shells as has been done by McDougall,[2] we obtain a theoretical $n^* = 1.68$. The difference between this and 1.63 is small and the difference between the Landé-Fermi-Goudsmit result and the theoretical one is therefore significant. For $3p$ the theoretical $n^* = 2.26$ and the experimental $= 2.12$. It is vital to orthogonalize the series electron functions to the core functions in computing $\mu$ and $\Delta\nu$ because $\overline{1/r^3}$ and $\overline{(1/r)(dV/dr)}$ are sensitive to the amplitude of the functions at small $r$. The factor due to this correction is approximately 14 for $3p$.

The effects discussed should similarly be sensitive to perturbations by configurations involving excitation of core electrons. A calculation of the first-order effect of a perturbation of $(2s)^2(3p)$ by $(2s)(3s)(3p)$ changes the theoretical h.f.s. value by about 8 percent and is not sufficient to matter materially. Similarly the effect of $(2p)^5(3p)^2$ on $(2p)^6(3p)$ is appreciable but not sufficient to bring about agreement. Effects on h.f.s. due to the first power of

coefficients of the perturbing configuration disappear by using Fock's field.[3]

The usual computation of nuclear $g$ factors is not necessarily wrong, but it is fair to say that it is uncertain on account of the sensitiveness of the theoretical values to perturbations.[4] We intended to postpone publication until sufficiently detailed calculations were made to ascertain the $g$ factors. Professor J. H. Bartlett kindly informed us that he and his co-workers[5] have made related calculations for $K$ using the Hartree field and for Na using Fock's field, and it seemed of interest to report the present state of our calculation.

The results of Shoupp, Bartlett and Dunn for $3s$, $3p$ are easily extended to $4s$, $4p$. We summarize in Table I their values, our Hartree field values, and our Fock field values for $4p$. The ratio $\psi_{3s}^2(0)/\psi_{4s}^2(0)=4.75$ by using Fock's functions, and 4.28 by using $Z_i Z_0^2/n^{*3}$. For Hartree′, Fock′ it was supposed that the ratio of the h.f.s. and the multiplet

TABLE I.

| | | $3s$ | $3p_{3/2}$ | $4p_{3/2}$ |
|---|---|---|---|---|
| $a$ | Experiment[7] | 0.029 | $8.3\times10^{-4}$ $(7.5\times10^{-4})$ | $1.87\times10^{-4}$ |
| | Hartree | 5.85 | 22 (20) | 10.4 |
| | Fock | 2.5[6] | 5.1[6] (4.6) | 3.1 |
| $\mu$ | Goudsmit-Fermi[7] | 2.0 | 2.8 (2.6) | 2.0 |
| | Hartree′ | | 3.3 (3.0) | 2.4 |
| | Fock′ | | 3.1[6] (2.9) | 2.3 |
| | Hartree | | 2.6 cm$^{-1}$ | 1.2 cm$^{-1}$ |
| $\Delta\nu$ | Fock | | 10.7[6] | 4.0 |
| | Experiment | | 17.2 | 5.49 |

frequency separations is given correctly by the respective functions of Hartree and Fock. The ratio of the two frequency differences as obtained from experiment was then equated to its theoretical value which involves $\mu$ and hence $\mu$ was determined. This amounts to defining an effective $Z_i$ by $\overline{Z_i}=-(dV/rdr)/\overline{(1/r^3)}$ where $V$ is the potential of the central field, and by using this $Z_i$ in Goudsmit's[8] Eq. (6). The Hartree and Fock values of $Z_i$ are 8.91 and 8.54. The first of these was communicated by us to Ellett and Heydenburg.[7] The $Z_i$ and $\mu$ thus determined are insensitive to progressive errors in the computation of the wave function and depend essentially on its shape for small $r$. They may be expected to be nearly the same for any central field calculation. The values of $\mu$ obtained by means of this $Z_i$ will be correct if there exists a central field which suffices for the discussion of the hyperfine and the ordinary fine structures; they may be wrong if there are pertubations affecting the multiplet and h.f.s. structures unequally.

The values marked[6] were kindly supplied to us by Shoupp, Bartlett and Dunn.

Values of $\mu$ obtained[8, 9] from $6s$, $6p$, $7p$, $8p$ of Cs check each other satisfactorily. Measurements of Wood and Fortrat on the principal series of Na disagree with the Landé gross doublet formula while for K, Cs the formula holds well. There is thus some evidence that Na is a poor element for testing the theory. The difference between $\mu$ $(3p)$ and $\mu$ $(4p)$ may be due, however, partly to experimental error as is seen by comparing values in each row of the $3p$ column.

College of the City of New York, L. A. WILLS
University of Wisconsin, G. BREIT
April 14, 1935.

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[7] A. Ellett and N. P. Heydenburg, Phys. Rev. **46**, 583 (1934).
[8] L. P. Granath and R. K. Stranathan, Phys. Rev. **46**, 316 (1934); Bull. Am. Phys. Soc. April 25–27 (1935); Paper 80.
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## The Magnetic Moment of the $Na^{23}$ Nucleus

From the most recent experiments with sodium[1–6] it has been concluded that the nuclear spin $I=3/2$ and that the total h.f.s. splitting[1] for the $3\,^2S_{\frac{1}{2}}$ state is 0.0583 cm$^{-1}$, for the $3\,^2P_{3/2}$ state 0.0050 cm$^{-1}$, and for the $3\,^2P_{\frac{1}{2}}$ state 0.0083 cm$^{-1}$. Ellett and Heydenburg, using formulae developed by Goudsmit[6] and Fermi and Segré,[7] have calculated values of the nuclear magnetic moment. From the $3\,^2S_{\frac{1}{2}}$ state, they find $\mu=2.02$ nuclear magnetons; while from the $3\,^2P$ states, they obtain $\mu=2.3-2.6$ n.m. Hartree wave functions were used by Wills and Breit,[8] who obtained values $\mu=5.8$ and $\mu=22.6$ from the $S$ and $P$ states, respectively. Since, however, their calculations show the multiplet splitting for the $^2P$ state to be 2.60 cm$^{-1}$, as compared with the observed value of 17.6 cm$^{-1}$, it is fairly obvious that better wave functions than those of Hartree are needed for accurate calculations. It is the purpose of this note to investigate whether or not the functions recently published by Fock and Petrashen[9] will serve the purpose.

The h.f.s. separation of a $^2S$ state is $\Delta(s)=(8\pi/3)\{(2I+1)/I\}\mu\mu_0\psi^2(0)$; that of a $^2P_{3/2}$ state is $\Delta^2P_{3/2}=(8/3)\{(2I+1)/I\}\mu\mu_0\overline{(1/r^3)}$. The gross structure separation for the $^2P$ state is[7] $\delta=(3\mu_0^2/hca_0^3)\overline{(1/r)(dU/dr)}$, where $U(r)=-11/r+V(r)$, and $V(r)$, is tabulated by Fock and Petrashen.

We find the following results: $\lim_{r\to0}(f_{3s}/r)=2.86$; $\overline{(1/r^3)_{2p}}=0.144$; $\overline{(1/r)(dU/dr)_{2p}}=1.23$; from $^2S$, $\mu=2.5$ n.m.; from $^2P$, $\mu=5.1$ n.m.; and $\delta=10.7$ cm$^{-1}$. The values of $(1/r)(dV/dr)$ are given in Table I.

TABLE I.

| $r$ | $\frac{-1}{r}\frac{dV}{dr}$ | $r$ | $\frac{-1}{r}\frac{dV}{dr}$ | $r$ | $\frac{-1}{r}\frac{dV}{dr}$ | $r$ | $\frac{-1}{r}\frac{dV}{dr}$ |
|---|---|---|---|---|---|---|---|
| 0.00 | | 0.24 | 147 | 0.60 | 23.1 | 1.4 | 3.43 |
| .02 | 2400 | .26 | 123 | .65 | 19.9 | 1.5 | 2.84 |
| .04 | 1700 | .28 | 105 | .70 | 17.2 | 1.6 | 2.37 |
| .06 | 1300 | .30 | 90.0 | .75 | 15.0 | 1.7 | 1.99 |
| .08 | 987 | .32 | 78.1 | .80 | 13.2 | 1.8 | 1.69 |
| .10 | 747 | .34 | 68.5 | .85 | 11.6 | 1.9 | 1.44 |
| .12 | 571 | .36 | 60.7 | .90 | 10.2 | 2.0 | 1.24 |
| .14 | 441 | .38 | 56.2 | .95 | 9.12 | 2.2 | ↓ |
| .16 | 345 | .40 | 49.2 | 1.0 | 8.04 | 2.4 | $\overline{10}$ |
| .18 | 273 | .45 | 39.2 | 1.1 | 6.37 | ↓ | $\overline{r^3}$ |
| .20 | 220 | .50 | 32.4 | 1.2 | 5.17 | | |
| .22 | 179 | .55 | 27.1 | 1.3 | 4.20 | | |

It is seen that the introduction of the Fock functions serves to improve the calculated value of the $^2P$ multiplet splitting very much. If one assumes the ratio $\overline{(1/r^3)}_{3p} : \overline{(1/r)(dU/dr)}_{3p}$ to be approximately the same for the Hartree and Fock functions, then this means that $\mu\delta$ is also approximately the same. For the Hartree case, $\mu\delta = 58.8$; for the Fock case $\mu\delta = 54.6$. If we suppose that this latter value is not very different from that which would be obtained with exact wave functions, and that the present theory of multiplet separations is correct, then it is permissible to use the experimental value of $\delta$ and to solve, and one obtains $\mu = 3.1$ n.m.

The agreement between the value $\mu = 2.5$ n.m. from the $^2S$ state and the estimated value $\mu = 3.1$ n.m. from the $^2P$ state seems to indicate that the true value of the magnetic moment of the $Na^{23}$ nucleus lies in this neighborhood. It may be remarked that our method of estimation seems capable of yielding good results for $p$ electrons even with a rather poor wave function (such as Hartree's), but that accurate results for $s$ electrons will probably be obtained only with quite accurate wave functions, as may be seen by comparing the values $\mu = 5.8$ (Hartree function) and $\mu = 2.5$ (Fock function).

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J. H. Bartlett, Jr.
C. G. Dunn

Department of Physics,
University of Illinois,
April 9, 1935.

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